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# **ECOLOGY AND ANALYSIS**

## **OF TRACE CONTAMINANTS**

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ORNL  
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Ecology and Analysis  
of  
Trace Contaminants  
Program

### **PROGRESS REPORT**

**OCTOBER 1974 - DECEMBER 1975**

**OAK RIDGE NATIONAL LABORATORY**

OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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ECOLOGY AND ANALYSIS  
OF TRACE CONTAMINANTS

PROGRESS REPORT  
OCTOBER 1974—DECEMBER 1975

Editors

R. I. Van Hook  
W. D. Shults

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FEBRUARY 1976

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OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37830  
operated by  
UNION CARBIDE CORPORATION  
for the  
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION





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## 1. INTRODUCTION

This is the fourth and final progress report<sup>1-3</sup> of Oak Ridge National Laboratory's Ecology and Analysis of Trace Contaminants (EATC) Program which is supported by the Environmental Aspects of Trace Contaminants Program of NSF/RANN. The overall objective of the EATC program has been to develop techniques, information, and understanding which will be useful to government agencies, industry, and the scientific community in assessing the environmental impact of trace amounts of toxic substances and in reducing discharges of certain of these. The work has not been specific to any one trace contaminant although much of our effort has been focused on trace elements. However, some work has been directed at trace organic compounds in natural water and at characterizing both the organic and inorganic constituents of materials from coal-conversion pilot plants.

EATC research encompasses five areas: (1) development and application of a Unified Transport Model for trace contaminants; (2) ecological research to characterize the translocation and accumulation of trace elements in the environment; (3) measurements research to improve analytical efficiency and capability; (4) development of advanced aqueous abatement technology featuring recycle and recovery; and (5) information flow and management. Progress made during this reporting period (September 1974 - December 1975) is detailed in Sections 3-7 and is briefly summarized in Section 2.

During this reporting period the work has revolved about four project themes: (1) studies of the input, distribution, and outflow of trace elements to Walker Branch Watershed at ORNL from neighboring coal-fired power plants; (2) studies of the transport, distribution, and ecosystem effects of Pb, Cu, Cd, and Zn on the Crooked Creek Watershed near a lead smelting-mining complex in the New Lead Belt of southeastern Missouri (a joint effort with the University of Missouri-Rolla, NSF/RANN New Lead Belt Project under the direction of Dr. Bobby G. Wixson); (3) investigation of the transport and biological accumulation of mercury in the Holston River-Cherokee Reservoir system in Virginia and Tennessee; and (4) analytical characterization of materials from various coal-conversion pilot plants. These project themes constitute realistic situations for testing of techniques and, in addition, provide an opportunity to obtain useful information on important pollution problems.

#### References

1. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants, Progress Report June 1972 - January 1973, ORNL-NSF-EATC-1 (March 1973).
2. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants, Progress Report January 1973 - September 1973, ORNL-NSF-EATC-6 (January 1974).
3. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants, Progress Report October 1973 - September 1974, ORNL-NSF-EATC-11 (December 1974).

## 2. SUMMARY

A major effort in the Ecology and Analysis of Trace Contaminants program has been concerned with the development of a Unified Transport Model (UTM) which can be used to describe and predict the transport and fate of trace contaminants through the atmospheric, terrestrial, and aquatic environments. In concept the air, land and aquatic systems are represented by three major model components, designed to be run in sequence. In practice we have developed a suite of compatible submodels that can be assembled into a UTM to meet specific user requirements (i.e., to meet researcher needs or management needs). This research has required evaluation and modification of existing models, development of new models, and application of the UTM and/or its components--all proceeding simultaneously. The following paragraphs highlight first our developmental activities and then applications of the UTM during the current reporting period.

We have rewritten the deposition subroutine of the Atmospheric Transport Model (ATM), improved the ATM to obtain faster calculations and better input/output formatting, and provided for different types of vegetative cover and episodal events. A separate subroutine was incorporated that treats distant (> 50 km) depositions. A model (SULCAL) that deals with atmospheric sulfur behavior has been developed; it can be used as a stand-alone model.

The UTAH and ARIZONA soil chemistry models were examined for potential incorporation into the UTM, and three other transport

submodels have been developed. These include a theoretical plate ion-exchange model, a soil-plant-atmosphere-water model (PROSPER), and an analytical model for analysis of soil moisture and trace contaminant transport (ODMOD). The submodels SCEHM, CERES, and DRYADS, which interface with PROSPER, are used to examine and predict the effect of plant water status on plant growth and solute transport. SCEHM treats the deposition, infiltration, exchange and flow of heavy metals in soils. CERES describes forest stand growth, and DRYADS treats contaminant uptake by leaves via gaseous diffusion.

A point source model, PNTSRC, has been incorporated into the water component of UTM, simulating the industrial discharge situation. SEDTRN, a stream channel sediment transport model, has also been merged with the Wisconsin Hydrologic Transport Model (WHTM) to form CHNSED.

A digital topography code was developed for watershed characterization purposes; it is useful for determining basin divides and directions of flow. Our optimization code, ORTRM, has been generalized and applied to parameters dealing explicitly with trace contaminants. OPTRM was used to study potassium transport in the Walker Branch Watershed with the important finding that significant improvement in results are obtained by optimizing on only two parameters if they are closely related to the transport process.

Other studies at Walker Branch Watershed include the use of ATM to compute depositions and air concentrations for eighteen elements for comparison with measured results. Also the WHTM was used to simulate cadmium streamflow in Walker Branch, with excellent results

for summer months but poorer results for winter and spring months when water flow is large.

We have continued our study of the transport and fate of Cd, Cu, Pb and Zn deposited on the Crooked Creek Watershed in the New Lead Belt Region of southeastern Missouri. This has been a collaborative activity with the NSF/RANN supported team at the University of Missouri-Rolla. For the water year 1974, the WHTM predicted outflows of Pb, Cd, Cu and Zn that are in best agreement with measured data for Zn, which is the metal that is most nearly represented chemically by current model assumptions. Inclusion of solubility limitations will provide closer agreement between observed and simulated values for both Cu and Cd.

We also used the soil chemistry model (SCEHM) to simulate the transport of Pd, Cd, Cu and Zn at a ridge top site on the Crooked Creek Watershed and found that agreement between computed and measured results is best for those metals that tend to remain uncomplexed in the soil solution.

Finally, it should be mentioned that the UTM and its components have been applied to a variety of problems during this reporting period. Four examples merit special mention. ERDA used the UTM to help evaluate the transport and fate of trace contaminants from anthropogenic sources associated with the development of fossil-energy facilities. The ATM was used by ERDA and TVA to estimate  $SO_x$  concentrations in the atmosphere near coal-fired steam plants. The State of New York is using the atmospheric and hydrologic components

of the UTM to evaluate the effects of road salting. Lastly, the U. S. Forestry Service has used the UTM to study the effects of various timber harvesting alternatives on water yields at the Coweeta Hydrologic Laboratory.

The Ecological Research component of EATC has focused on development and application of techniques for evaluating trace element impacts on the environment. This has been accomplished through studies of transport, fate, and effects of chlor-alkali plant wastes in the Holston River, coal-fired power plant emissions on Walker Branch Watershed, and lead smelter emissions on Crooked Creek Watershed. Distribution and transport studies of Hg on  $<44 \mu$  size sediment particles in the Holston River indicate a significant input of Hg into the Cherokee Reservoir. Analysis of Hg and  $\text{CH}_3\text{Hg}$  concentrations in fish and benthic invertebrates in the Holston River show elevated levels below the waste disposal site. The Hg levels in fish and invertebrates tend to follow the concentration of Hg in the water column and bed sediments. Analysis of volatile Hg in the air mass over the waste disposal site indicates values just below EPA ambient air standards for gaseous Hg suggesting volatile Hg as a significant pathway of Hg dispersion from this waste disposal site.

Studies of atmospheric input and hydrologic output of trace elements on Walker Branch Watershed have improved our estimates of annual deposition of elements such as Cd and have aided in identifying the sources of these metals. Development and use of new precipitation samplers which seal positively and minimize exposed metal surfaces



to reduce contamination have resulted in reducing the atmospheric input estimate for Cd of 62 g/ha to 9 g/ha which is in much better agreement with results of the ATM calculations. Elements for which the ATM showed poor correlation between calculated and measured depositions appear to be attributed to automotive sources (Br and Pb) or long-range transport of fine particulates (Cd, Hg, Se). Those elements for which there was general agreement between ATM calculations and measured values appear to be those coming from adjacent coal-fired power plants. In estimating landscape output of trace metals through stream water, the use of discharge-weighted averages has emphasized the composition of stream water during periods of high flow rate thus better representing the composition of total monthly discharge.

Our work on Crooked Creek Watershed has demonstrated an accumulation of  $O_2$  litter, elevated levels of heavy metals, and a reduction in the decomposition process, all apparently due to emissions (Cd, Pb, Cu, Zn,  $SO_x$ ) from the adjacent lead smelter. This reduction in decomposition has altered the leaching of macronutrients in the litter and soils and may result in reduced forest productivity. We hypothesize that the area affected by the smelter is increasing due to the chronic contaminant input. The evidence obtained during our one-year study supports this hypothesis, but is not adequate to fully test it.

Our work in x-ray fluorescence continued through June 1975. We improved the mathematical techniques used in converting fluorescence

signals to concentrations by incorporating corrections for interelement effects. We verified the use of a borate fusion technique for preparation of nonhomogenous samples. Preliminary experiments were completed in which an intense polychromatic irradiation source (synchrotron) was evaluated for XRF analysis; a signal to noise gain of ten was observed when compared with conventional polychromatic sources. Monoenergetic sources are still preferable to polychromatic sources, and we have provided much information on the use of monoenergetic sources to the academic and industrial communities.

Much progress was made during this reporting period in our Mass Spectroscopy Research project. We have developed the multi-element isotope dilution technique for use with spark source mass spectrometry and applied the procedures to a number of sample types. Computer software for data handling and computation was developed. Chemical and spectroscopic conditions were established and the method was successfully applied to the analysis of gasoline, gasoline additives, fuel oil, water samples, dust, animal tissues,  $^{233}\text{UO}_2$  and various alloys. In general, if  $10^{-9}$  g of an element and a spike can be placed on the SSMS electrode, its concentration can be determined with an error of less than 10%. The spiking solution for aqueous samples contains  $^{204}\text{Pb}$ ,  $^{196}\text{Hg}$ ,  $^{183}\text{W}$ ,  $^{106}\text{Cd}$ ,  $^{97}\text{Mo}$ ,  $^{77}\text{Se}$ ,  $^{67}\text{Zn}$ ,  $^{65}\text{Ca}$ ,  $^{61}\text{Ni}$ ,  $^{57}\text{Fe}$ ,  $^{53}\text{Cr}$  and isotopically normal Er. Mononuclidic elements (e.g., As and Co) are compared with the enriched isotope of nearest mass.

We also initiated work with the ion microprobe mass analyzer (IMMA) during this reporting period, but the short project duration is limiting accomplishment in this project. We have studied two approaches to the quantification of IMMA data. One is based on computer programs that correct IMMA data via computing sensitivity factors for the elements of interest. This approach suffers from the fact that IMMA data are very dependent upon sample matrix, and suitable standards are not generally available. The second approach that we have studied briefly is the use of isotope dilution for IMMA analyses. We observe signals for each element, but this approach is limited thus far by our inability to prepare substrates or areas of measurement that are truly representative of the original sample. The IMMA is unsurpassed, however, in its ability to present spatial distribution data for a wide range of elements on a tiny surface.

Gas chromatographic research has continued with emphasis on the applicability of our GC-microwave excited spectrometric detector system, and on the characterization of materials deriving from coal-conversion technologies. Major accomplishments include (1) the development of a method for determining parts per trillion amounts of  $\text{CH}_3\text{HgCl}$  in water; (2) the development of a method for determining alkylarsenic acids; (3) demonstration of the utility of GC-MES for selectively determining silicon-containing compounds; (4) application of multi-component gas chromatographic profiling methodology to coal-derived materials; and (5) the development of profiling techniques for the polynuclear aromatic hydrocarbons in complex samples.

Studies of the sulfur-bearing constituents in synthetic crude oils were also carried out.

Liquid chromatography research continued to emphasize the use of high-pressure LC for separating and detecting low volatility organic constituents in natural and polluted waters. During this period water samples from a large metropolis, an algae culture, and an estuary were studied. Additionally, aqueous effluents from a coal conversion pilot plant and from the (chlorinated) cooling tower of an electric power station were examined. Some preliminary experiments were conducted to explore the use of HPLC for separating and detecting organo-phosphorus compounds in natural and/or process waters; more than 60 compounds were observed in a filtered water sample taken from an algal growth.

The objective of our work in the abatement technology area has been to develop and assess two promising techniques for the removal and recovery of contaminants from various industrial waste streams. These techniques are (a) solvent extraction with high molecular weight amines and (b) electrochemical reduction using electrodes of large surface area. During this reporting period we completed studies of the solvent extraction of zinc and cadmium, and published our findings. We have studied the removal and recovery of zinc and cyanide from industrial electroplating effluents, and have thoroughly investigated several promising flowsheets in our laboratory-scale miniplant. Excellent removal and recovery of zinc and cadmium can be obtained and amine losses to the raffinate are small; chemical

reagent costs are low; the treated water may be recycled to eliminate a large fraction of the total effluent volume. More than 600 inquiries have been received in regard to this work, primarily from the industrial sector.

Our studies of electrolytic recovery of dissolved heavy metals with porous and packed-bed electrodes have led to design, construction, and testing of two types of prototype metal-recovery cells. One of these may be used for continuous recovery of mercury from chlorine plant process streams or other effluents without the use of added reagents and without formation of mercury-bearing precipitates. The mercury recovery cell may be operated continuously, allowing periodic removal of liquid mercury from the cell for recycle. Feasibility studies on removal of dissolved silver from photographic processing solutions provided data which were used for design of a practical-sized metal-removal cell. This modular metal-removal cell is part of an integrated, closed-cycle metal-recovery system which also includes rinse cabinets and an electroplating metal-recovery cell. This recovery system is designed to treat 1,000 to 10,000 gal/day of industrial effluents or process streams of various types. Metal is recovered in the form of a solid sheet, which may be recycled to plant processes.

Our Toxic Materials Information Center (TMIC) is continuing to provide support services for the EATC Program through 1) creation of data bases and answering inquiries on trace contaminants, 2) preparation and publishing bibliographies, 3) establishment of a pilot

project on tabulating environmental data, 4) preparation and dissemination of the NSF/RANN Trace Contaminants Directory and Trace Contaminants Abstract, 5) maintenance of a directory of persons engaged in trace contaminants in the United States and several foreign countries, 6) dissemination of information on specific profiles to members of the EATC Program, and 7) other support activities including data and document acquisition for EATC personnel.

### 3. THE UNIFIED TRANSPORT MODEL

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N. M. Larson, R. J. Luxmoore, J. K. Munro,  
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#### 3.1 Introduction

The Unified Transport Model (UTM) has been developed to allow simulation of the transport, accumulation, and redistribution of trace contaminants in the environment. Thus the UTM structure draws the knowledge of many disciplines together into an objective state-of-the-art description of the transport and fate of trace contaminants through the atmosphere and terrestrial and aquatic ecosystems.

In concept, the air, land, and aquatic systems are represented by three major model components, designed to be run in sequence. The atmospheric component is based upon a Gaussian plume model and calculates deposition rates of aerosols for any point within a watershed. Concentrations of airborne aerosols at ground level are also calculated. The model includes consideration of point, area, line, and windblown sources for air pollutants. Deposition occurs by dry fallout and also by washout caused by rain falling through the plume. Air concentrations and depositions depend upon source strength, atmospheric stability, and wind speed and direction patterns. The spatial resolution of the atmospheric module now extends to a

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<sup>a</sup>Task Leader.

radius of 50 kilometers from any point source. One can use the model to simulate larger areas by constructing a mosaic of sub-area calculations. An extension of the model considers chemical changes of airborne  $\text{SO}_x$  with time. The deposition values calculated by the atmospheric model are used for input to the land component of the UTM.

The basic assumption underlying the land component of the UTM is that water is the major carrier of material through the terrestrial system. Thus, trace material transport can be modeled by combining hydrologic calculations with consideration of the chemistry of trace materials in aqueous media. Briefly, the terrestrial component is structured to receive atmospheric wet- and dryfall input to a watershed canopy and then simulate its movement until it is discharged in streamflow. The model simulates the amount of material washed from the canopy to the land surface during rainfall and allows for the exchange and uptake or adsorption of materials on surface soil. Surface runoff and scouring of soil particles are considered together with leaching of trace elements into the soil profile. An experimentally derived equilibrium distribution coefficient is used to estimate the concentrations of contaminants in subsurface soil water. This estimated concentration and the rate of soil water drainage are combined to estimate a subsurface input to the stream channel.

Finally, the outputs from the terrestrial component of the UTM enter the channel component, where flows are routed using a kinematic wave approximation. This portion of the program simulates transport



of dissolved and particulate materials in streamflow. Suspended and bedload transport are considered by the model. Mixing and exchange between the aqueous and solid phases for the particular chemical species of concern are also simulated. If point-source discharges of known strength are released to the stream, the channel component is capable of simulating their introduction and subsequent transport.

The UTM comprises a collection of programs that represents a tool for both research and management. The utility of the UTM to researchers lies in its ability to provide detailed estimates of variables that are too difficult or expensive to measure routinely, and as a convenient tool for developing and testing hypotheses. For the manager, the UTM provides a way to examine alternative management policies through simulated scenarios. However, one must recognize that a single model seldom satisfies the needs of both researchers and managers at the same time. We have met that challenge by developing a suite of compatible sub-models that can be assembled into a UTM for research needs or a different UTM for management-type studies.

3.1.1 Model Composition. Figure 3.1 illustrates the suite of programs that may be used in assembling a unified transport model to address a specific problem. Rather than attempt to describe all the possible combinations of submodels that could make a UTM version, Table 3.1 presents a brief description of each model component shown in Figure 3.1, together with a list of other submodels they depend upon. One can easily see the logical combinations of submodels once

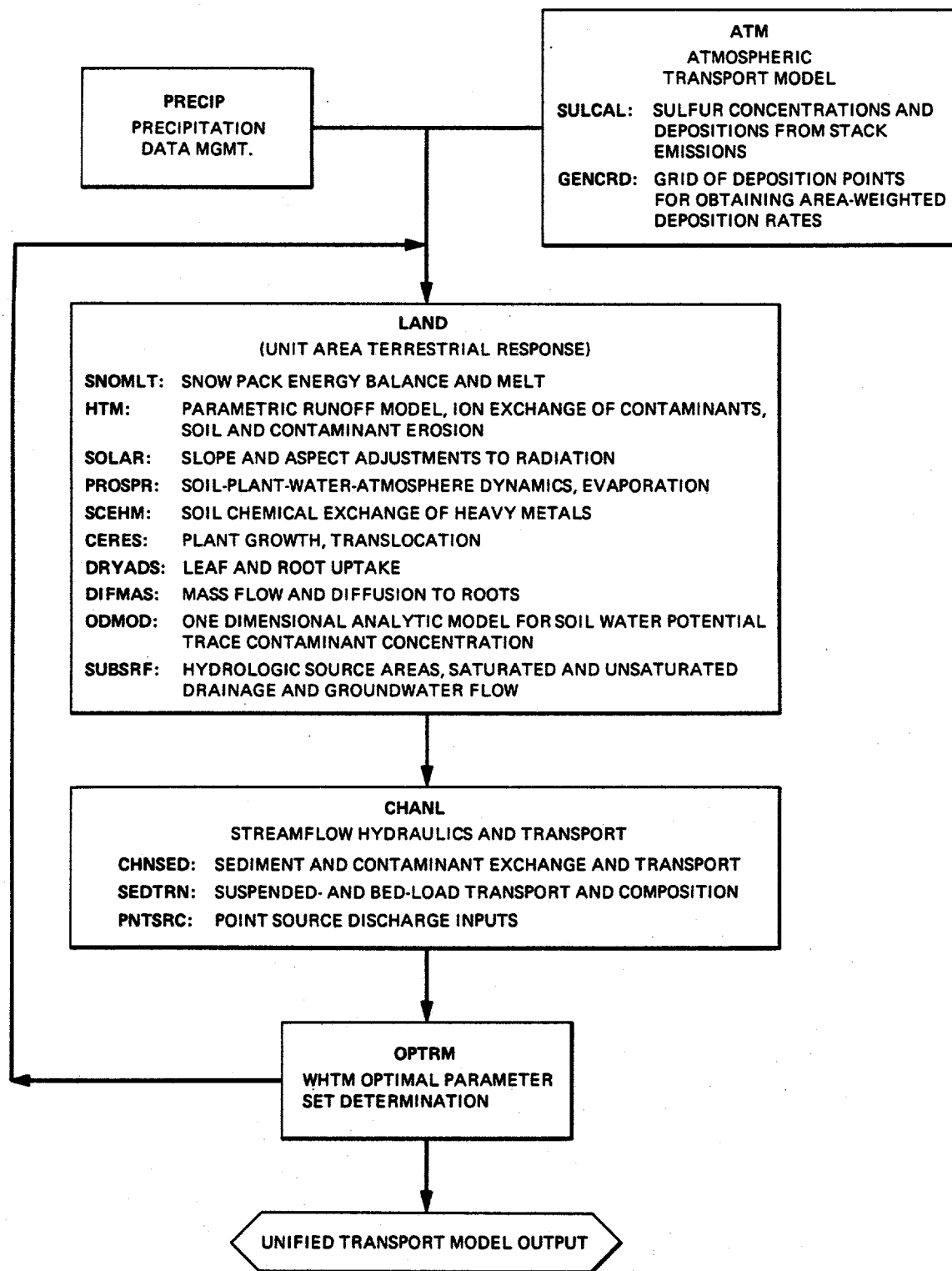


Figure 3.1 The submodels that may be linked to form a unified transport model.

Table 3.1. Program components of the Unified Transport Model

Model Name	Model description and linkages
ATM	Calculates the atmospheric transport and concentration, and wet and dryfall deposition of trace contaminants originating from point sources, area sources, line sources, and windblown sources. Operates as stand alone model (monthly resolution) or linked with PRECIP.
CERES	Calculates plant growth and respiration, standing crop biomass of leaves, stems, fruits and roots, and storage pools of sugars, live tissue, and dead or woody tissue. Also computes translocation of carriers (transpired water and phloem sugar movement). Has been used with the linked PROSPR-LAND package.
CHNSED	Calculates sediment transport and the exchange of contaminants between water and mobilized sediments in open channel flow. Depends upon the HTM-CHANL linkage to derive water and sediment inputs. Uses SEDTRN model to compute amount and composition of bed and suspended sediment load. Could be used with the LAND-PROSPR-CHANL linkage.
CHANL	Calculates open channel flow hydraulics for natural channels and lakes or ponds, using a kinematic wave approximation. Generates hydrographs for as many as 3 locations in a basin with as many as 7 stream reaches. Depends upon specification of channel inflow rates at 30-minute intervals.
DIFMAS	Calculates mass flow of solutes carried by soil water to the root/soil interface, and allows for diffusion in response to a concentration gradient. Depends upon the PROSPR-CERES-SCEHM linkage for specifying soil water flow, root density, and solute concentrations.
DRYADS	Calculates the uptake of contaminants through leaves and roots and the uptake of gases by leaves. Depends upon the PROSPR-CERES-SCEHM-DIFMAS linkage.
GENCRD	An interactive program used to generate a rectangular or polar coordinate grid of sampling points for use as input for the ATM. The toxicant deposition rates computed by ATM and the coordinates for these sampling points can then be used to obtain deposition rate isopleths or to obtain an area weighted deposition rate for a land segment of arbitrary geometry.
HTM	Calculates runoff, erosion, and ion exchange and transport of contaminants and sediments to a stream channel (reach). It is based upon the Stanford Watershed Model, and runs as an integral part of the Wisconsin Hydrologic Transport Model (WHTM).
LAND	Control program for the terrestrial components of the UTM. Establishes climatic data files and accepts model parameters and initial conditions, and generates runoff input files for the aquatic component of the UTM. Depends upon PRECIP for water input, and can use deposition data from ATM.
ODMOD	Calculates soil water potential and concentration of trace contaminant in a many-layered pseudo two-dimensional soil. Operates as a stand-alone model.
OPTRM	Determines an optimal set of model parameters read by the LAND component of the UTM. An iterative execution of LAND and CHANL is used to minimize an objective function that quantifies the dissimilarity between observed and simulated flow or contaminant transport values.
PROSPR	Simulates atmosphere-plant-soil moisture relations on a day-to-day or hourly basis. Calculates soil water potential and content in as many as 8 soil layers, evapotranspiration, and plant water potentials. Operates as a stand alone model (daily) or in conjunction with LAND (hourly or quarter-hourly).
PRECIP	Accepts and creates files for precipitation and wetfall deposition data, and maintains a master inventory file for type and amount of data stored. PRECIP controls the assembly of the precipitation and deposition data that are input to LAND. Operates as a stand alone model or as an integral part of the WHTM or with the ATM.
PNTSRC	Allows the introduction of average daily point-source inputs of water and contaminants to any specified reach in the channel system. Depends upon CHANL for operation with the UTM.
SCEHM	Simulates the transport of heavy metals through the soil system in a forested watershed; including deposition, infiltration as a function of solubility, ion exchange, and mass transport in saturated and unsaturated drainage. Depends upon PROSPR, and is usually operated with PRECIP, ATM, and LAND.
SEDTRN	Computes sediment transport rate as both suspended and bed load material. Also calculates particle size composition of the sediment using an iterative procedure and the composition of stream bed materials. Operates as a stand-alone model with the driver code CH, using input flow data, or may be operated with simulated flow data provided by the CHNSED version of CHANL.
SNOMLT	Simulates the energy balance on a snowpack, including consideration of radiation (short- and long-wave), convection, advection, ground heat, and snowpack (thermal) quality. Depends upon LAND and PRECIP.
SOLAR	Adjusts daily observations of solar radiation for the slope and azimuth of a specified watershed segment and distributes the daily total into hourly increments based on solar altitude. Operates as a stand-alone model or together with LAND.
SUBSRF	Simulates runoff from hydrologic (variable) source areas, distributes unsaturated flow between stream input and deep soils, and estimates groundwater storage and flow. Depends upon the LAND-PROSPR linkage.
SULCAL	Calculates the rate of oxidation of SO <sub>2</sub> to various species of sulfate dissolved in aerosol droplets or in the form of particles of ammonium sulfate as a function of time and distance from the SO <sub>2</sub> source. Operates as stand-alone model or coupled to the ATM.

the basic conceptual structure of the UTM is understood. For example, when the ATM is linked with the HTM and CHANL, the combined model can be used to study the impact of new fossil-fuel/steam electric generating plants on atmospheric and aquatic concentrations of heavy metals. On the other hand, when the ATM is linked with mechanistic process models such as PROSPER, SCEHM, CERES, DIFMAS, and DRYADS, the combined version can be used for studies such as those at Crooked Creek Watershed in the new lead belt of Missouri, where the goal is the detailed examination of the buildup of heavy metals in the forest ecosystem and the effects the metals have on the biological processes associated with primary productivity and decomposition.

There are some missing links in many of the feasible UTM combinations. These gaps exist because of the limited set of problems it has been possible to address with the UTM thus far. Even though the EATC applications are ending, we anticipate future development and refinement of the programs as the UTM is applied to new problems both by ORNL staff working on other projects, and by outside users.

3.1.2 Representative Uses. The UTM has been applied to a wide variety of problems by various users. ERDA has used the UTM to help evaluate the transport and fate of trace contaminants from anthropogenic sources associated with the development of fossil-energy facilities. In that work, the complete UTM model was used because it was necessary to track materials from their appearance as atmospheric emissions from stacks, through nearby watersheds, and into

streamflow. However, some potential users are not concerned with the complete environmental transport question. For them, the individual components are most useful. For example, the atmospheric transport component of the UTM has been used by ERDA and TVA to estimate  $SO_x$  concentrations in the atmosphere near coal-fired steam plants. The atmospheric and hydrologic components of the UTM are being used by the State of New York Department of Environmental Conservation staff as a part of a study to evaluate the effects of road salt application. Finally, the hydrologic component of the UTM has been used by the US Forest Service to study the effects of various timber harvesting alternatives on water yield at Coweeta Hydrologic Laboratory in North Carolina.

3.1.3 Costs Associated with the UTM. One can identify three potential costs associated with using the UTM. They are the cost of model implementation, the cost of characterizing a study area and assembling the data necessary to conduct simulation studies, and the actual machine cost of conducting simulations for a specified situation. All three should be carefully weighed by a potential user.

A new user who wishes to implement and maintain the UTM on his own system should expect to spend at least six months establishing the model on his computer system and conducting a sufficient number of test simulations to become familiar with the model operating characteristics. Prior experience with the model could cut the time requirements to about a month. The UTM is IBM-360 compatible.

Because extensive file management capabilities are built into the code, translation to a different system such as Univac could be very time consuming. For example, transfer of the WHTM from a UNIVAC-1108 system to the IBM-360 system at ORNL required in excess of two man-years of effort.

Once the UTM has been implemented on a system, the next cost to consider is that associated with assembly of information for a specific study area. If all measurements have been made, then the time required to assemble the data may be estimated as follows: Climatic data seldom require more than a few days' effort to assemble, provided they have been reduced to at least tabular form from the direct observations. Soils and vegetation data can usually be assembled in a day or two. The most difficult data to compile are those concerned with trace contaminants. The time involved can range from a few days to several weeks or longer depending upon the situation. Physical parameters describing the watershed can be obtained from topographic maps and on-site inspection in a week or less. Thus, development of the data set necessary for conducting an annual simulation for a specific basin segment can often be accomplished with less than one month's effort, depending upon the availability of data.

Machine costs for conducting a simulation are usually the smallest part of the overall study expense. The version of the UTM which includes LAND, PROSPER, SCEHM, CERES, DIFMAS, and DRYADS requires about two minutes of CPU time on the IBM 360/91 per segment-

year simulated. The addition of streamflow and sediment routing adds about two minutes per reach per year simulated. Thus a basin with five segments and seven reaches in the stream channel system would require about 24 minutes of CPU time for a complete one-year simulation.

### 3.2 The Unified Transport Model: Implementation

Development and implementation of the three major components of the UTM are presented here. In Section 3.2.1, recent modification to the Atmospheric Transport Model, including the development of the sulfur chemistry submodel, are described. Section 3.2.2 contains a description of the Land component, including the various soil chemistry models (theoretical plate model, SCEHM, and ODMOD), the plant growth model CERES, the solute uptake model DRYADS, and the source area runoff model SUBSRF. Modifications to the Water component are described in Section 3.2.3, including the point source model PNTSRC and the CHNSED model, which simulates sediment transport in a stream channel system. Finally, the optimizing code OPTRM and the digital topography code are discussed in Sections 3.2.4 and 3.2.5, respectively.

3.2.1 The Air Component of the UTM. The Atmospheric Transport Model<sup>1</sup> (ATM) was first conceived to estimate deposition of various materials from numerous (as many as ten) point, area, and line sources. The model is subject to the constraint that the calculations, as well as preparations for calculations, be held to an absolute

minimum. A typical case involving four point sources, ten area sources (counties), and a few line sources (roads) requires less than five minutes of computer time on the IBM 360/91. These calculations provide twelve months of concentration and deposition estimates. The parameters for the problem include type of material (particulate or gas), density, size, settling velocity, deposition velocity, wind speeds, wind directions, atmospheric stabilities, volume and heights of materials emitted, and washout, deposition and resuspension factors.

Recent modifications to the model<sup>2</sup> include separate subroutines for the geometrical calculations, and further changes to provide faster machine calculations. Input and output have been reformatted into more logical and compact units. Control parameters have been introduced to permit printing of pre-selected sets of output.

The deposition subroutine has been rewritten to account for varying types of vegetative cover. The functions of terminal velocity and deposition have been separated and redefined in the updated model. For particles with terminal velocity greater than 0.01 m/sec, the plume is tilted to simulate the effect of gravity on the heavy particles.

Episodic exposures are calculated in subroutine MAXCON. This subroutine provides estimates of the worst possible set of meteorological conditions to affect a given location subjected to insult from numerous sources.



For distances beyond 10 km, the conventional deposition assumptions incorporated in the ATM begin to fail rather severely<sup>3</sup>, particularly when the total amount of remaining effluent is examined. Consequently a separate subroutine for distant deposition estimates (DEPLET) has been incorporated into the model. This subroutine assumes a steady-state solution in which the center line of the plume rises, subject to conservation of mass constraints.

The sulfur chemistry model, SULCAL, is a significant extension of the ATM. Because sulfur, which is released in the atmosphere in the form of  $\text{SO}_2$  and  $\text{SO}_3$  mainly through the combustion of fossil fuels, undergoes reactions in the atmosphere, it cannot be treated as an inert substance. Interactions occur among sulfur and atmospheric water, ammonia, carbon dioxide, oxygen, ozone, and the OH radical. The equilibrium distribution of the various resulting species present in the gas phase in aerosol droplets, and as particles, can be calculated from the temperature and the chemical rate and equilibrium constants. Using this equilibrium distribution, SULCAL calculates and sums the reaction rates associated with different kinetic pathways to find the net rate of oxidation of sulfur in the atmosphere.

We are using SULCAL in a stand-alone version to investigate the reaction pathways and disposition of sulfur as a function of atmospheric conditions. Table 3.2 summarizes a series of calculations with SULCAL that show the sensitivity of various output quantities (at 25 km from the source) to what are thought to be typical values for various input quantities. The underscored values are reference

Table 3.2. Sensitivity of concentrations and oxidation rate calculated by SULCAL to variation of input parameters

Input values <sup>a,b</sup>	Output values at 25 KM from stack <sup>c</sup>					
	SO <sub>2</sub> (10 <sup>-3</sup> mmol/m <sup>3</sup> )	Sulfate (10 <sup>-3</sup> mmol/m <sup>3</sup> )	SO <sub>2</sub> Ox. Rate <sup>d</sup> %/hr	Liq. Water (10 <sup>-3</sup> g/m <sup>3</sup> )	H <sub>2</sub> SO <sub>4</sub> in Droplets (mmol/g H <sub>2</sub> O)	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> in Droplets (mmol/g H <sub>2</sub> O)
Sulfur in Coal (Wt %)	2.5 1.0 0.5	14.3 6.0 3.2	19.3 7.9 4.0	↑ 3.2 ↑	7.7 3.1 1.6	2.5 2.4 2.4
Meteorological Stability Class	A C F	4.8 6.0 14.8	6.3 7.9 19.7	↑ 3.2 ↑	2.6 3.1 6.5	2.4 2.4 3.0
Wind Speed (m/sec)	1 2 4 8	9.8 6.0 3.5 2.0	25.3 7.9 2.5 0.84	↑ 3.2 ↑ ↑	9.0 3.1 1.0 0.32	2.8 2.4 2.2 1.7
Ambient OH (10 <sup>-8</sup> mmol/m <sup>3</sup> )	10 2 0.5 0.1	3.9 6.0 6.4 6.6	28.2 7.9 3.0 1.6	16.0 3.2 0.8 0.16	11.2 3.1 1.2 0.60	2.5 2.4 2.3 2.1
Ambient NH <sub>3</sub> (10 <sup>-4</sup> mmol/m <sup>3</sup> )	20 6 2	↑ 6.0 ↑	↑ 7.9 ↑	↑ 3.2 ↑	3.0 3.3 2.5	2.3 2.5 0.33
Ambient Temp. (°C)	18.33 19.44 21.11 23.89 26.67 29.44	↑ ↑ 6.0 ↑	↑ ↑ 7.9 ↑	↑ ↑ 3.2 ↑	740 14 3.1 1.6 1.2 0.95	0.010 0.54 2.4 4.7 6.5 7.9
						0.0040 0.021 0.096 0.18 0.25 0.31

<sup>a</sup> Bold numbers are the reference values. Other values were taken one at a time, holding all other input values at the reference values.<sup>b</sup> Other input values were: Wt % carbon in coal = 82.6; Wt % Hydrogen in coal 6.9%; Combustion rate = 100 Kg coal/sec; Effective stack height = 400 m; Deposition velocity = 0.01 m/sec; ambient water concentration = 930 mmol/m<sup>3</sup>.<sup>c</sup> Concentrations are averages across the plume.<sup>d</sup> From reference 4.

values. Some of the output quantities for the reference case are plotted versus the distance from the source in Fig. 3.2. The other output quantities in the table result by varying each input quantity from its reference value while holding all other inputs at the reference values. For example, entries in the first row were generated using 2.5 wt % sulfur in coal, stability class C, wind speed 2 m/sec, OH concentration  $2 \times 10^{-8}$  mmol/m<sup>3</sup>, NH<sub>3</sub> concentration  $6 \times 10^{-4}$  mmol/m<sup>3</sup>, and temperature 21.11°C. Arrows in the table imply no change.

Under all conditions tested<sup>4</sup> only the OH radical is important in the oxidation of SO<sub>2</sub>; thus, the percentage of SO<sub>2</sub> oxidized per hour depends only on the ambient concentration of the OH radical. This concentration is controlled at the assumed values by unspecified chemical reactions. The amounts of SO<sub>2</sub>, sulfate, and condensed water in the plume vary directly as the sulfur content of the coal. The droplets contain mostly sulfuric acid with a relatively small amount of ammonium sulfate, which is equivalent to the assumed ambient concentration of ammonia. Increased wind speed strongly decreases the concentration of SO<sub>2</sub>, sulfate and liquid water. The ambient temperature, through its strong inverse effect on the relative humidity, greatly affects the amount of condensed water and the concentrations of acid and ammonium sulfate in the aerosol droplets. Details of the SULCAL model and results of additional calculations are described in another report<sup>5</sup>.

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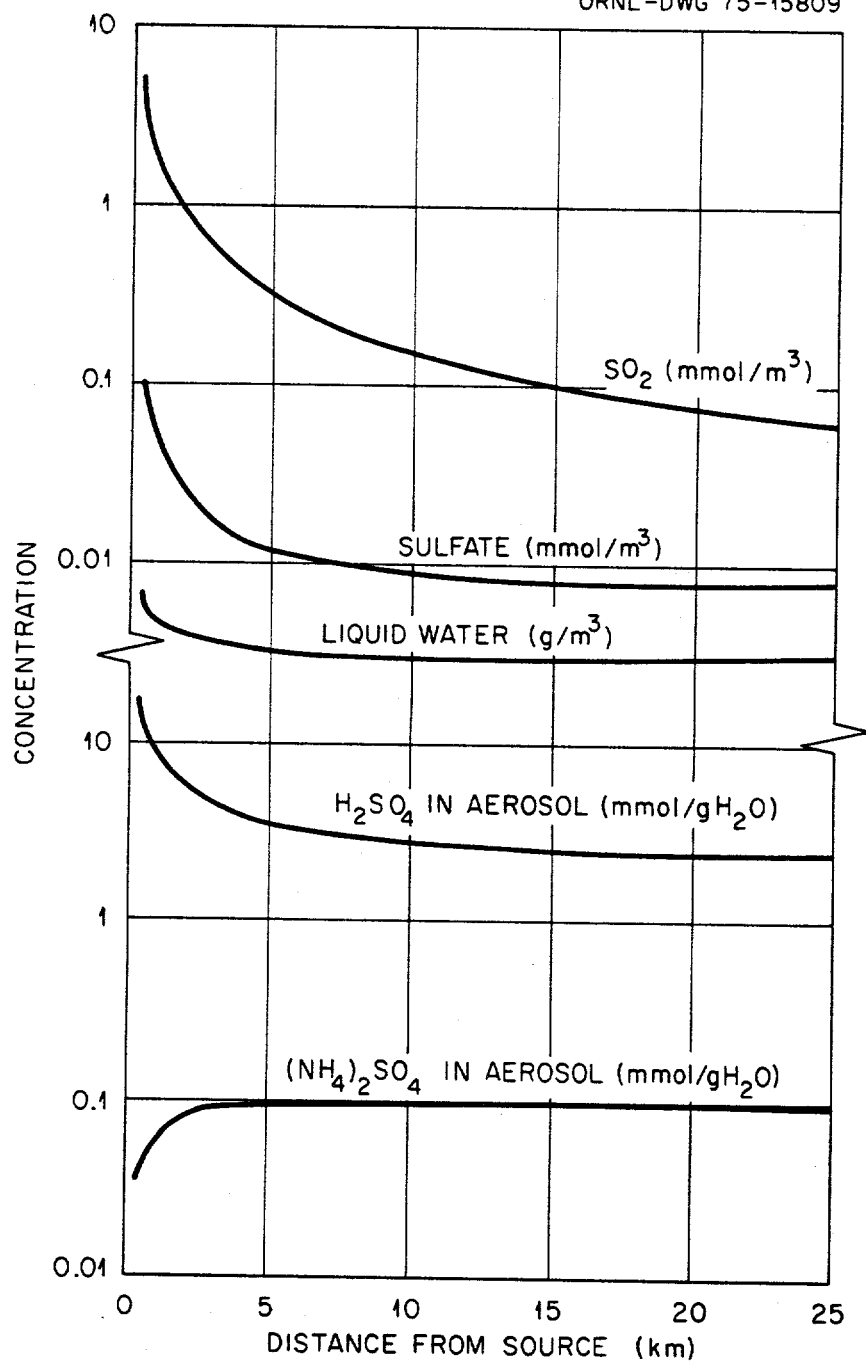


Figure 3.2 Concentrations as a function of distance from the source, as calculated by SULCAL for the reference case (see Table 3.2).

SULCAL has been incorporated as an option into the Atmospheric Transport Model submodel phase of the UTM. Additional data required to invoke the SULCAL option of the ATM include properties of the combustion and scrubbing process, chemical composition of the coal burned, atmospheric temperature and ambient concentrations of  $\text{SO}_x$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{O}_2$ ,  $\text{O}_3$ , and  $\text{OH}$ . In many cases the program will insert nominal values if details are not known. The merged ATM-SULCAL model is described in detail elsewhere<sup>6</sup>.

3.2.2 The Land Component of the UTM. Various submodels for transport of trace contaminants have been incorporated into the UTM. Two existing soil chemistry models were examined, and three different models have been developed. These models differ in complexity, in sophistication of approach, in data requirements, in region of applicability, and in computer requirements.

The theoretical plate ion-exchange model, developed for use in the WHTM, has been described in the WHTM user's manual<sup>7</sup>. In this model, water enters the four theoretical plates in units of an integral number of single plate volumes during a given time interval. Mass balance considerations require that some (left-over) water be added to the incoming water during the next time interval; a recent correction to the model applies mass balance considerations to the solute as well.

The two existing soil chemistry models which were studied for possible incorporation into the UTM were the UTAH model of J. J.

Jurinak et al.<sup>8</sup> and the ARIZONA model of G. R. Dutt et al.<sup>9</sup>. The UTAH model and its limitations have been described in a previous progress report<sup>10</sup>. The ARIZONA model includes routines which describe the exchange of  $\text{Ca}^+ - \text{Mg}^{++}$ ,  $\text{Ca} - \text{Na}^+$ , and  $\text{Na}^+ - \text{NH}_4^+$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and the flow of solutes.

The UTAH and ARIZONA models were the foundation for building a suitable model for the transport and exchange of heavy metals in soils (SCEHM)<sup>11</sup>. In particular, the methodologies for describing solute transport and for defining soil chemistry layers came from the ARIZONA model. SCEHM, which is designed to be run with PROSPER, considers the deposition, infiltration, exchange, and flow of heavy metal contaminants (Figure 3.3). The contaminants are considered to be deposited as both wetfall and dryfall onto the litter layer from interception storage. Experimentally determined solubility constants for each heavy metal form the basis for estimating losses from litter to infiltration and surface runoff, which occur through dissolution of the contaminants. Once within a soil layer, exchange of the heavy metal is assumed to take place instantaneously and the amount exchanged depends on measured distribution coefficient,  $K_d$ . Within a soil layer, the ratio of water flux to water content is assumed to be the same as the ratio of the solute flux to the solute. This assumption is used to calculate contaminant fluxes associated with horizontal and vertical water flow. Calculations are done on an hourly basis unless water is infiltrating. In that case calculations are done for every fifteen minutes of simulated time. Balances

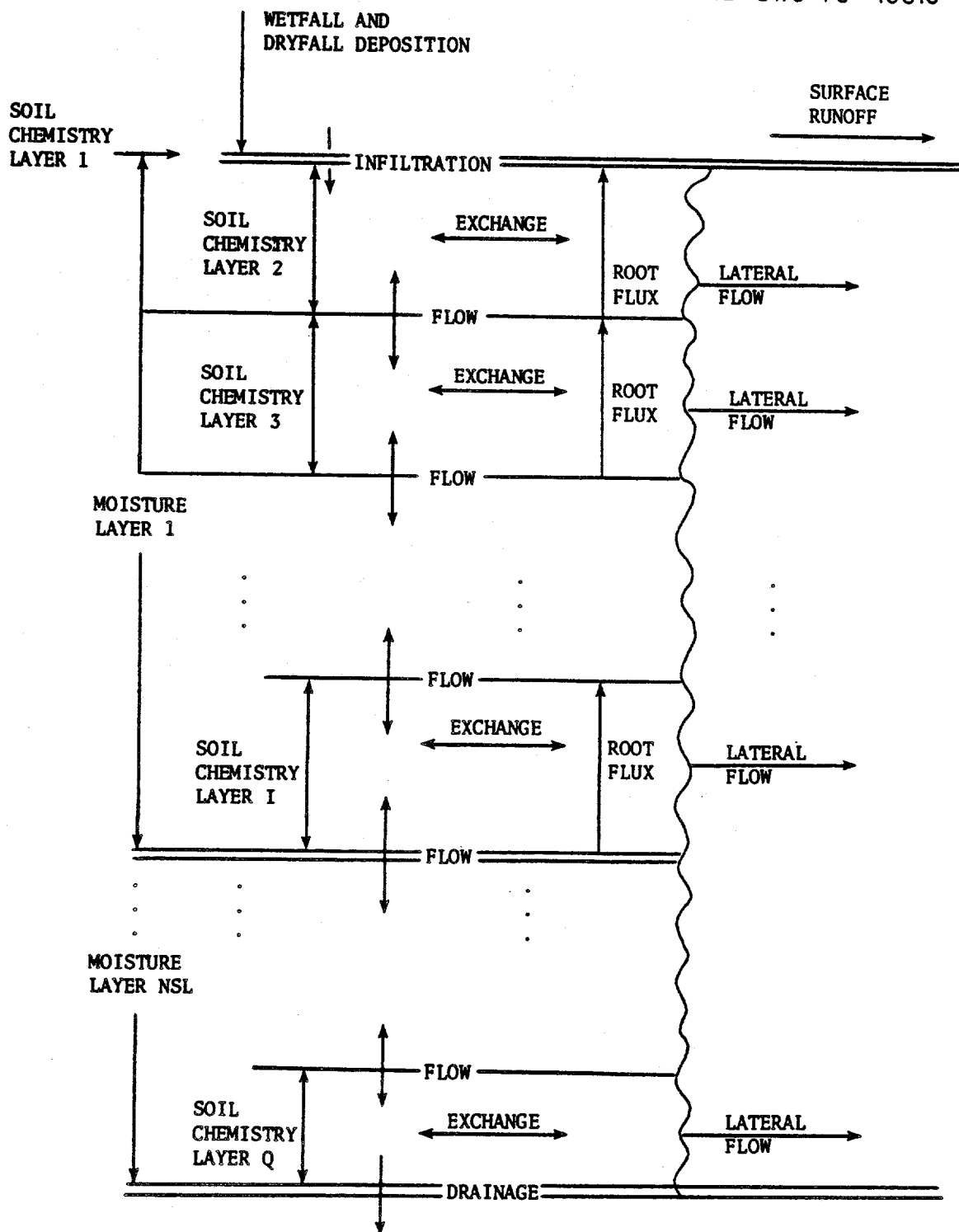


Figure 3.3 The sequence of deposition, infiltration, exchange, and flow of heavy metal contaminants considered in SCEHM.

for each phase are updated at each time step, and monthly summaries are printed.

An analytical transport model (ODMOD) has been developed to predict the coupled movement of both water and trace contaminants through a layered, unsaturated soil-moisture zone. In order to achieve computation speeds suitable for watershed applications, moisture properties of the soil are approximated as exponential functions of pressure head. Lateral flows are treated as sinks in a basically vertical one-dimensional analysis. In addition, only advection by the Darcy flow velocities and linear adsorption by the soil matrix are considered in depicting movement of the trace contaminant. Details of both the analytical and the numerical solutions to the soil-moisture and trace-contaminant equations are presented in another report<sup>12</sup>.

A model has been developed to incorporate the variable hydrologic source area concept<sup>13-20</sup> into the UTM. This model (SUBSRF) includes two simultaneous processes which together produce increased streamflow during storms. First, the perennial channel system expands to several times its original length by extending into zones of low moisture storage capacity, which quickly saturate and produce surface runoff during storms. Secondly, as the channel network grows, it intercepts an increasing amount of subsurface drainage and direct precipitation. When SUBSRF is linked to PROSPER and SCEHM in the UTM, the combined program will represent an alternative to the WHTM formulation now used for complete heavy metal transport simulations.



CERES<sup>21</sup>, a forest stand growth model, and DRYADS<sup>22</sup>, a contaminant uptake model, have been developed to simulate plant growth and solute uptake. CERES is coupled to PROSPER, and DRYADS is linked to PROSPER, CERES, SCEHM, and DIFMAS.

The primary purpose of CERES is to simulate stand growth and sugar and water transport within plants, in order to predict both short-term effects and long-term accumulation of trace contaminants in a forest. Plants are divided into leaf, stem, root, and fruit compartments (Figure 3.4) with transport of sugar substrate among

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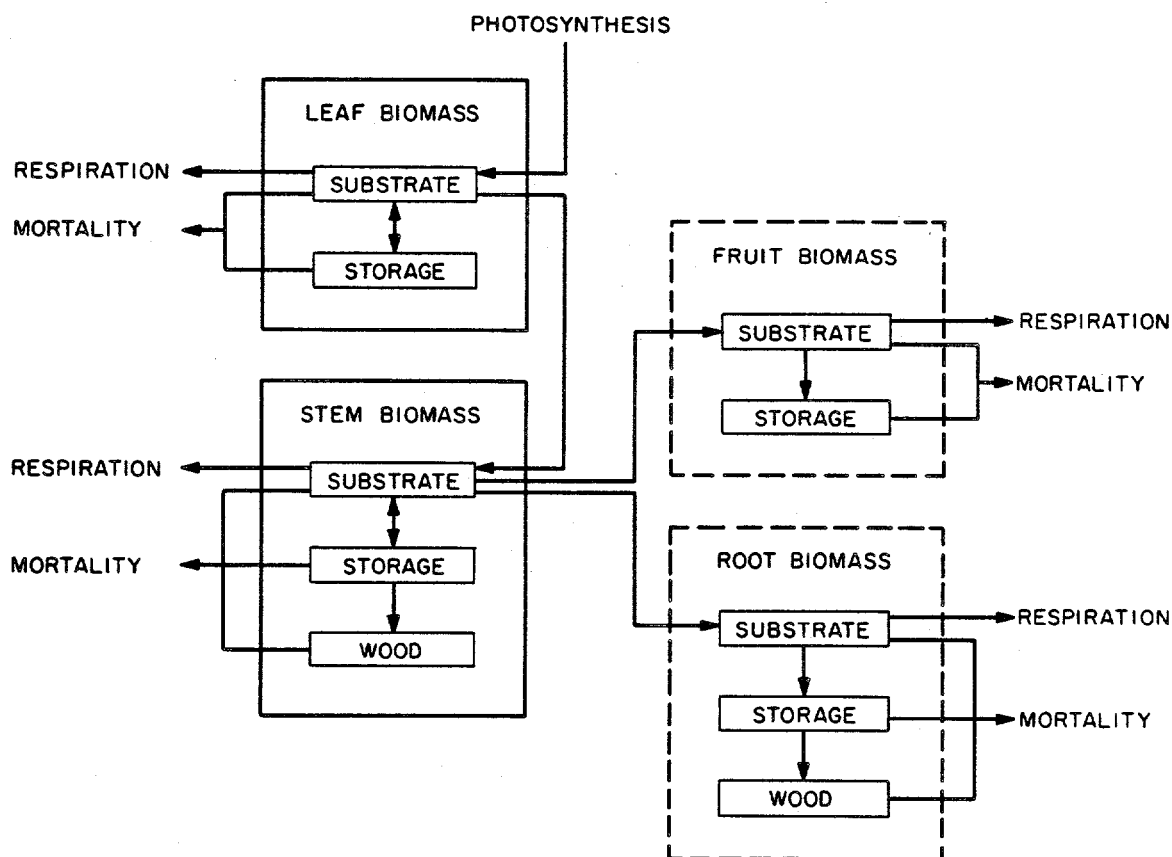


Figure 3.4 The leaf, stem, root, and fruit compartments of plants considered in CERES.

compartments occurring in the phloem tissues. Transport depends upon the sugar substrate concentration differences between compartments<sup>23</sup>.

An important feature of the CERES model is its ability to interface with the soil-plant-atmosphere-water model PROSPER as a means of both predicting and studying the effects of plant water status on growth and solute transport. The rate of growth depends upon the CO<sub>2</sub> concentration inside and outside the leaf and the resistance to diffusion along that pathway<sup>24,25</sup>.

The PROSPER model estimates surface and boundary layer resistances, which are used in CERES to calculate hourly photosynthesis. Hourly water potential values from PROSPER are used to adjust the growth rate of new tissues to agree with data published by J. S. Boyer<sup>26</sup>. An example of short-term (hourly) effects (Figure 3.5) shows growth of leaf and root tissue occurring in the late afternoon when the plant water stress is reduced. The model also is capable of simulating long-term (seasonal and annual) effects on growth (Figure 3.6) and trace contaminant accumulation when interfaced with DRYADS in the Unified Transport Model.

Subroutine DRYADS simulates the uptake of contaminants into leaves by gas diffusion through stomata and by diffusion through the leaf cuticle. Uptake also occurs by solute movement into roots. The movement of contaminants within the vegetation is coupled to the transpiration stream from roots to stems and leaves, and to the sugar phloem pathway for the downward flux from leaves to roots.

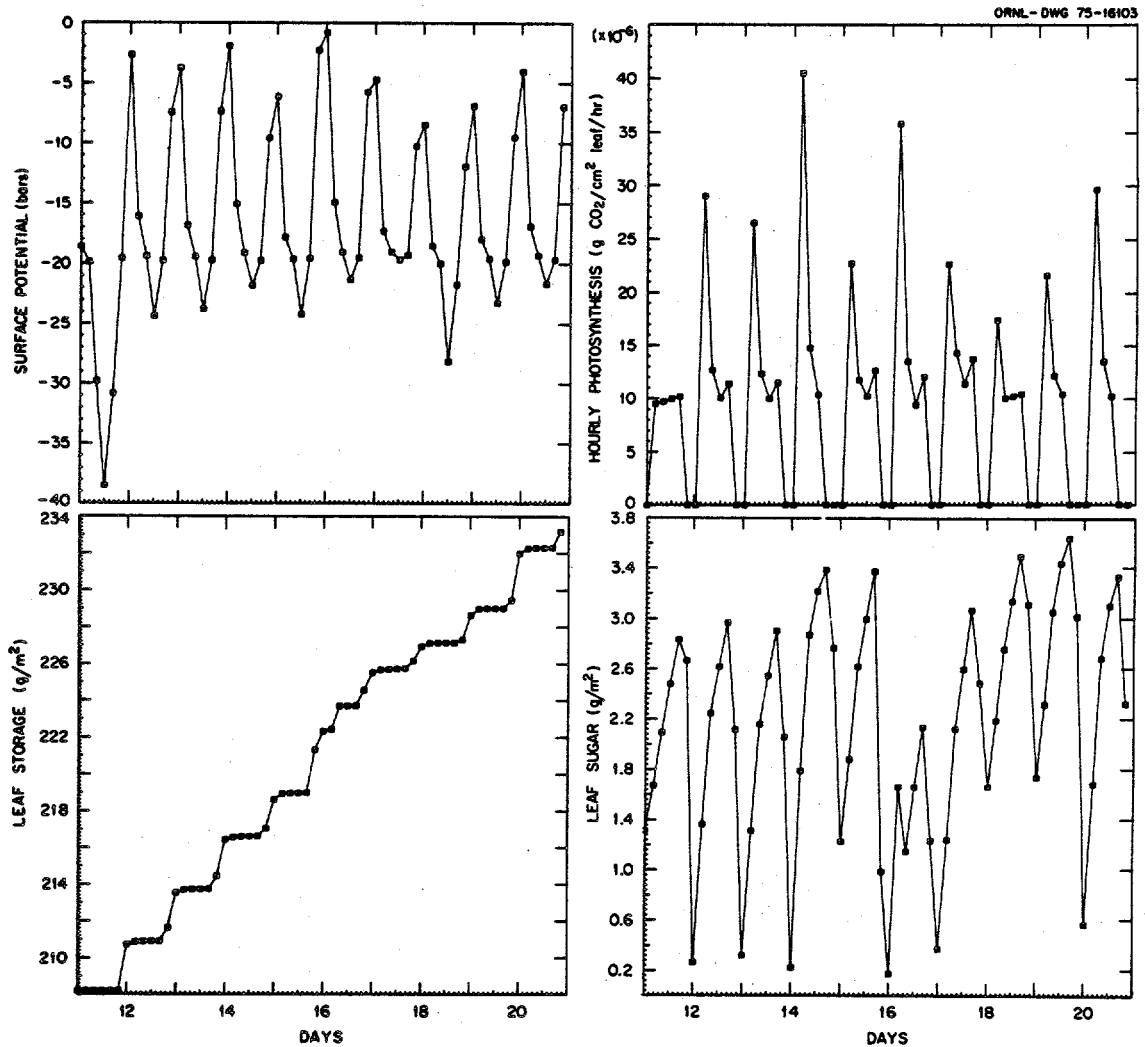


Figure 3.5 Hourly patterns of surface potential, photosynthesis, leaf sugar and leaf storage from the CERES-PROSPER Model showing reduced leaf growth (storage) during periods of low water potential.

DRYADS depends heavily on the coupling of several other routines. A link with the ATM, LAND, and PROSPER is necessary. A mass flow and diffusion model, DIFMAS, provides the link between DRYADS and SCEHM. DIFMAS uses the algorithm of Baldwin, Nye, and Tinker<sup>27</sup> to calculate the amount of plant uptake. Transfer of data to DRYADS is shown in Table 3.3. Figure 3.7 illustrates the complete coupling of the PROSPER, CERES, SCEHM, DIFMAS, and DRYADS models.

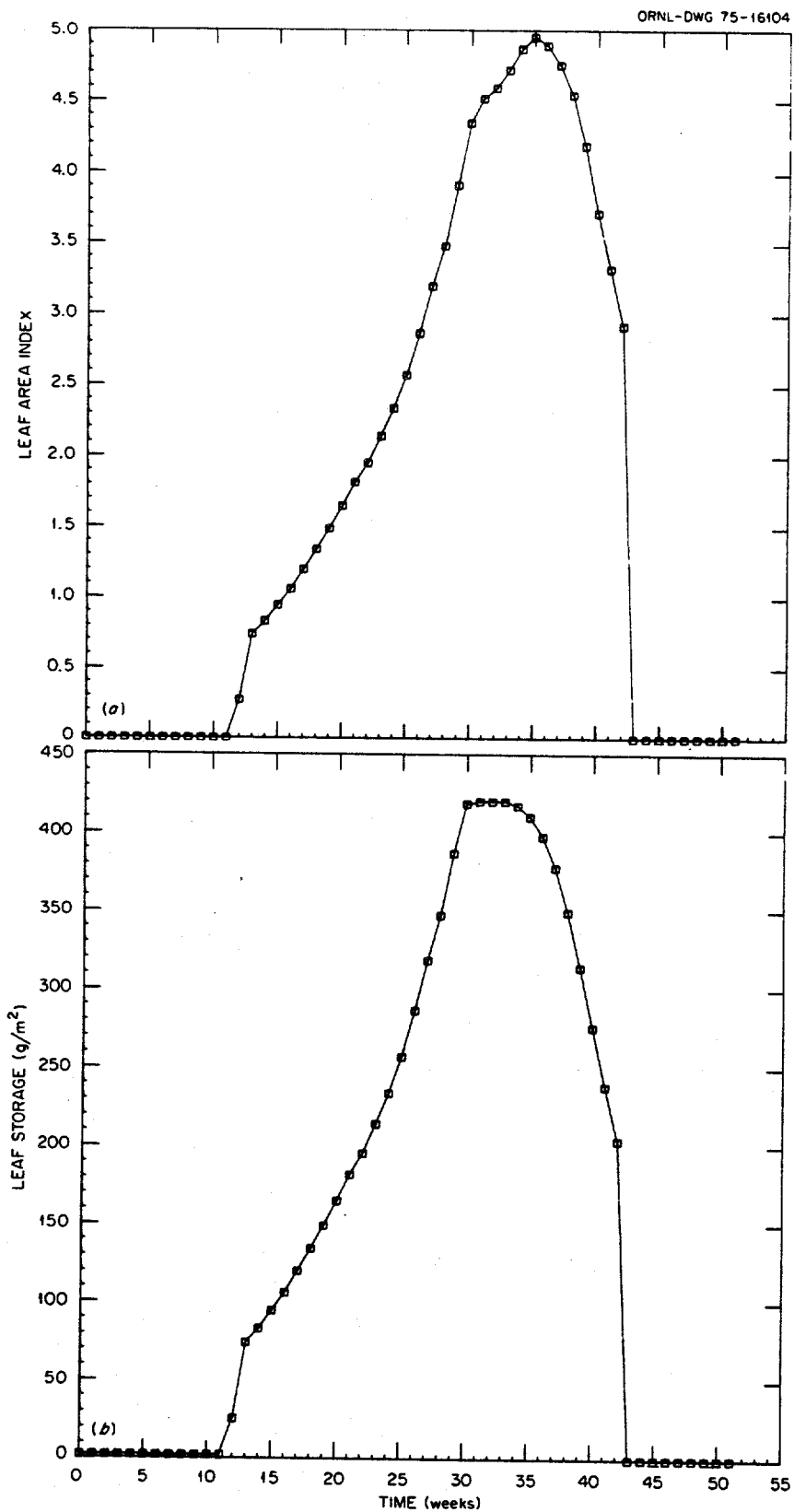


Figure 3.6 Seasonal patterns of leaf storage and leaf area index from the CERES plant growth model.

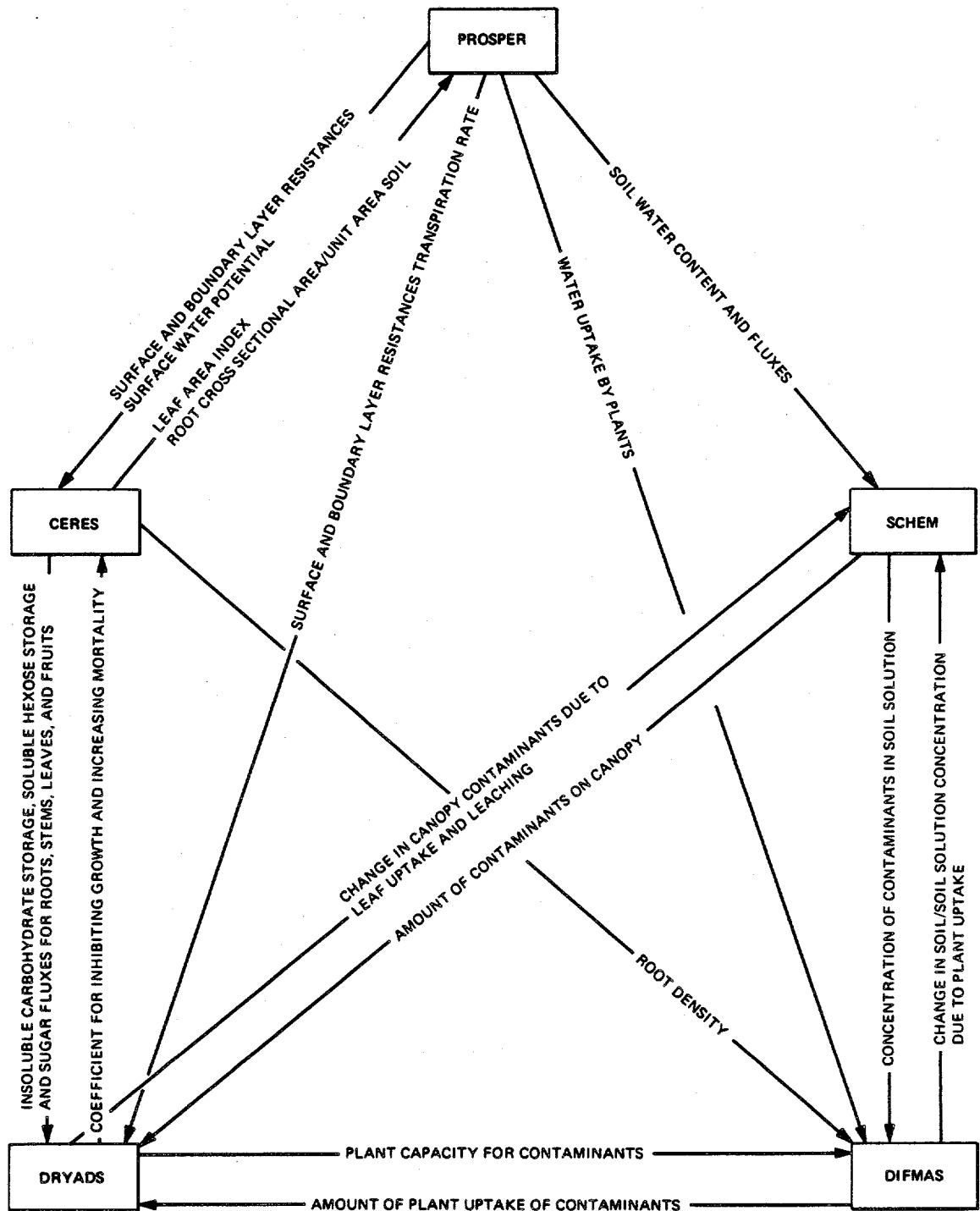


Figure 3.7 Coupling of the PROSPER, CERES, SCEHM, DIFMAS, and DRYADS submodels.

Table 3.3. Data transferred from coupled subroutines and their recipient processes in subroutine DRYADS

Coupled subroutines (data transferred)	DRYADS (processes involved)
1. <i>ATM</i> (air transport model) dryfall deposition gas concentration	cuticular uptake gas diffusion uptake
2. <i>LAND</i> (terrestrial hydrology) precipitation wetfall interception storage	solute leaching from leaves cuticular uptake cuticular uptake
3. <i>PROSPER</i> (soil-plant-atmosphere water flow) transpiration rate	solute transport from roots to stems and leaves
4. <i>CERES</i> (plant growth model) vegetation biomass vegetation growth rate sugar translocation rate	solute capacity of vegetation change in solute demand solute transport from leaves to stem & roots
5. <i>DIFMAS</i> (flow of solutes to roots) solute flux to roots	root uptake of solutes

Calculations made in DRYADS are on a fifteen-minute or hourly basis as determined by the time step used in subroutines LAND, PROSPER and SCEHM. When the accumulation of solutes in the vegetation from the atmosphere and soil solution builds up to toxic levels, a feedback loop from DRYADS causes growth rate processes in CERES to be reduced. The model structure also has application to situations where solute deficiency may be involved. The web of coupled subroutines is constructed to simulate the many interrelated chemical, physical, and physiological functions which affect both the primary productivity and the transport of toxic materials in a terrestrial ecosystem. The model is suitable for examination of the effects of episodic events on terrestrial ecosystems (e.g., storms, pulse SO<sub>2</sub> releases, rapid buildup of contaminants), where rapid rates of deposition, gas diffusion, or water flow are involved.

3.2.3 The Water Component of the UTM. The point source model PNTSRC has been implemented into the UTM. This model treats point sources of water and toxicant entering directly into the channel network. The primary function of this model is to simulate industrial discharge into streams. An alternate version of PNTSRC permits simulation of many land segments by treating outflow of water and contaminants from the upland portions of a watershed as point-source input for the downstream part of the basin.

A model of sediment transport in a stream channel system (SEDTRN)<sup>28</sup> has been written and merged with the WHTM; the resulting model is called CHNSED<sup>10,29,30</sup>. Particulate mobilization (sheet erosion and overland transport) and dissolved contaminant transport (associated with runoff, interflow, and baseflow inputs to the channel system) are considered in CHNSED. Following entry into the channel system, dissolved contaminant transport is linked with streamflow routing. Routing of the adsorbed fraction is controlled by sediment transport dynamics and is governed by bed load and suspended load transport, which is modeled in the SEDTRN portion of the code.

Sediment in as many as twelve size classes is separated conceptually into three components: sediment resident on the bed stream; sediment in transit as bedload; and sediment in transit as suspended load. CHNSED has also been modified to cope with sediment size fractions of density less than 1.0 (i.e., floating particles).

The model uses Manning's equation to determine flow rate and modifications to Stokes' law to calculate particulate fall velocity for both viscous and inertial particle settling. In the inertial fall region, the inertia of the fluid displaced by the falling particle as it settles must be considered, and the fall velocity is lower than that predicted by Stokes' law. It was discovered that the equation found in the literature<sup>31</sup> expressing the sedimentation velocity of sediment in water as a function of particle size in the inertial fall region is in error. Using experimental fall velocities<sup>31,32,33</sup>, the correct relationship has been determined and implemented in CHNSED. Figure 3.8 shows the fall velocity of quartz spheres in centimeters/second as a function of particle diameter, as simulated in the CHNSED model. The dashed lines indicate the computed dependence of fall velocity on nominal sediment diameter at various temperatures from 10°C to 50°C for sediment size classes of diameter less than 0.24 millimeters and at 20°C for sediment classes of larger diameter. The solid line and crosses represent data taken at 20°C by Allen<sup>31</sup> and Hazen<sup>33</sup>, respectively.

Our application of CHNSED to Walker Branch Watershed has been described in oral presentations<sup>34,35</sup> and will be mentioned in Section 3.3.2 of this report. Documentation for the approach used in CHNSED<sup>36</sup> gives detailed instructions for its application. This report also contains results of application of SEDTRN to sediment transport simulation in the Rio Grande River system, using published data<sup>37,38</sup>.



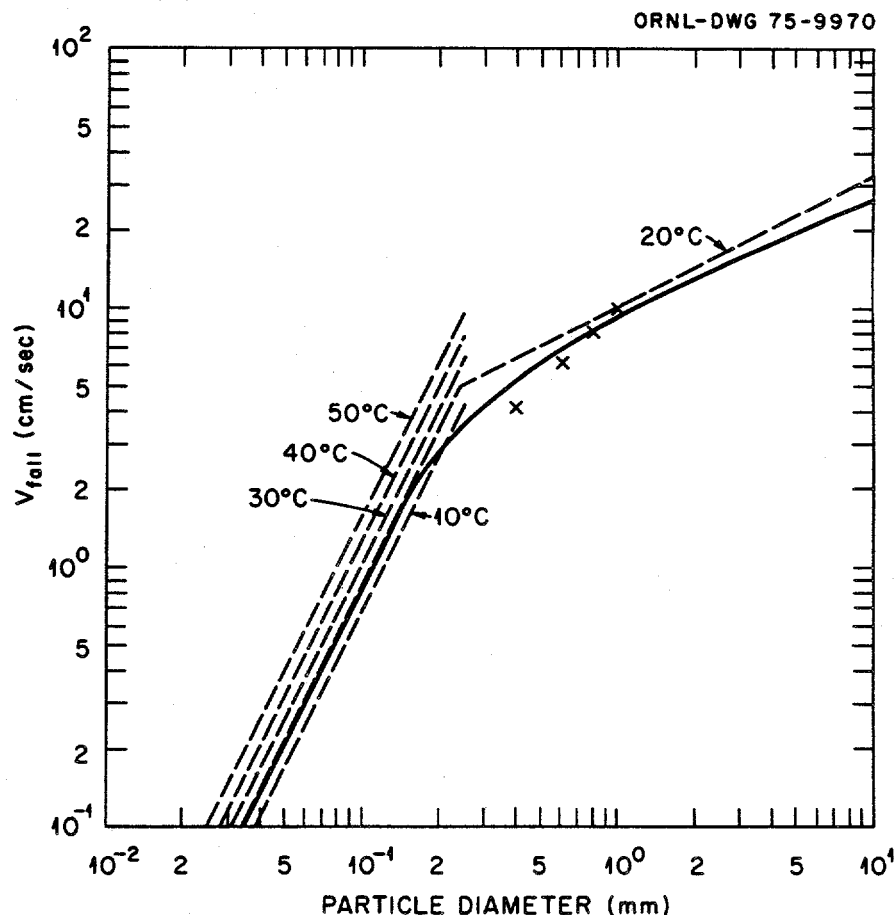


Figure 3.8 The relationships between fall velocity, particle diameter, and temperature for quartz spheres.

3.2.4 An Optimizing Transport Model (OPTRM) Code. The version of the Wisconsin Hydrologic Transport Model (WHTM) with parameter set optimization capability (OPTRM) has been briefly described in a previous progress report<sup>39</sup>, and is documented and available<sup>40</sup>. Since that time the model has been generalized and has been applied to parameters dealing explicitly with trace contaminant transport. Its application to the simulation of trace contaminant on Walker Branch Watershed is discussed in Section 3.3.2 of this report. Figure 3.9 illustrates the flow of control in the OPTRM code. As

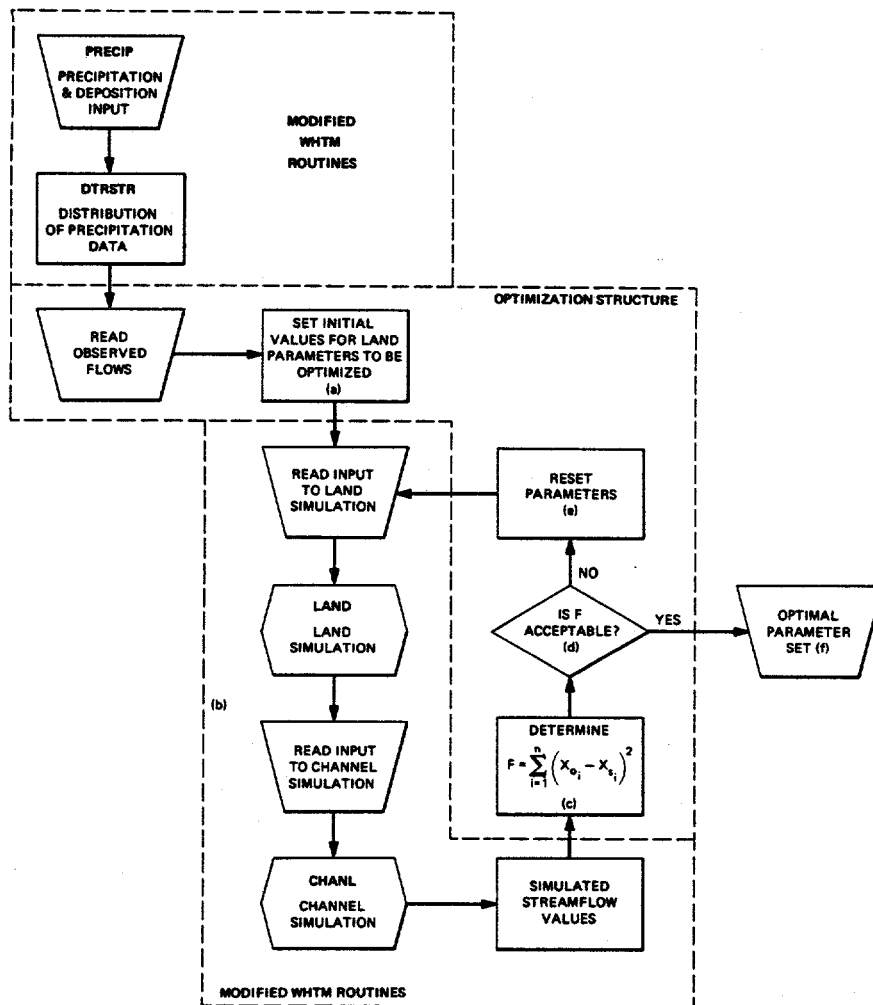


Figure 3.9 Schematic representation of OPTRM.

shown there, the PRECIP and DRTSTR links of the WHTM code are not modified for use in OPTRM. However, the LAND and CHANL simulation links in block (b) of the diagram lie within the optimization structure. Parameters mentioned in blocks (a) and (b) are those parameters related to water or trace contaminant transport that are read by the code in the LAND simulation link. The residual function  $F$  is calculated in block (c) and is defined by the equation

$$F = \sum_i^m (X_{o_i} - X_{s_i})^2$$

where  $X_{o_i}$  = the  $i$ th observed value, and

$X_{s_i}$  = the  $i$ th simulated value.

This function expresses the lack of agreement between the observed flow ( $X_o$ ) and the simulated flow ( $X_s$ ) of either water or trace contaminant. The sum is taken over  $m$  successive simulation periods (typically days or months). Flows are defined as quantities measured or simulated at the output of the CHANL system. The acceptability decision performed in block (d) is based on the percentage change of the residual function since the previous iteration. If the residual function has reached a nearly constant value, compared with the last iteration, then the value of  $F$  is considered acceptable and the optimal parameter set is identified (see function block (f)). In each execution of the OPTRM code the PRECIP and DTRSTR links are executed only once while the LAND and the CHANL links are executed several times. The number of iterations and therefore the execution time is determined by the number of parameters optimized, the accuracy of the initial trial solution, and the sensitivity of the model to the parameters being determined. The sensitivity of the simulated variables to various parameters guides the choice of the set of parameters to be optimized. The number of these parameters should be kept as low as possible. Typically, an execution of OPTRM with

25 - 50 iterations yields a final parameter set having a residual differing by less than 10% from a minimum value.

3.2.5 Digital Topography. A computer code<sup>41</sup> has been developed to use digital topographic information to characterize a watershed. This code estimates the WHTM parameters for drainage area and mean terrain slope, as mentioned in an earlier progress report<sup>39</sup>. Elevations at specified grid intervals are generated from digitized data, using an interpolation procedure based on an idea by R. L. Jones of NASA<sup>42</sup>. First, a plane tangent to the surface at each data point is determined. Then the elevation of a grid point is approximated by the weighted average elevation of tangent planes through the eight contiguous data points. Finally, a smoothing procedure is used to eliminate local anomalies. The code also determines and plots flow paths, including major stream channels within the watershed.

### 3.3 The Unified Transport Model: Applications

3.3.1 Application of the UTM to Crooked Creek Watershed in the New Lead Belt. The Crooked Creek Watershed (CCW) is located in the New Lead Belt Region of southeastern Missouri and is adjacent to the AMAX lead smelter and the Magmont lead mine. In cooperative studies with the NSF/RANN-supported New Lead Belt Study at the University of Missouri (Rolla), staff members of the Environmental Sciences Division have determined the transport, distribution, and fate of Cd, Cu, Pb, and Zn deposited on the CCW landscape following

emission from both the mining and smelting operations. Data obtained from these studies have been used to provide estimates of parameters required in applying the UTM to CCW. A primary objective of this application is to simulate the transport of the heavy metals through the watershed for several successive years to determine their accumulation and residence times in various parts of the watershed.

Hourly precipitation and climatological data sets for more than four successive years, from January 1971 to the present, have been assembled. Most of these data were supplied by Mr. George Carr, the environmental officer for the AMAX Smelting Company. J. C. Jennett of the New Lead Belt Project at the University of Missouri, Rolla (UMR), has supplied us with hourly precipitation, stream flow, and concentrations of the heavy metals Pb, Cd, Zn, Cu, and Mn in filtered and unfiltered stream samples for the watershed outfall for several storm events. The hourly precipitation data for these storms have been incorporated into the data obtained from a recording rain gauge at Viburnum, Missouri, located about five miles north of the watershed.

Geochemical and mineralogical studies by the UMR project group and measurements of the physical properties of the soil at selected sites in the watershed by C. Scrivner of the University of Missouri, Columbia (UMC), indicate that the original division of the watershed land area into segments according to the surface topography is not appropriate. A better choice is ridge top, ridge sides, and grassy meadow as shown in Figure 3.10. New hydrologic and toxicant data sets were prepared for these three land segments.

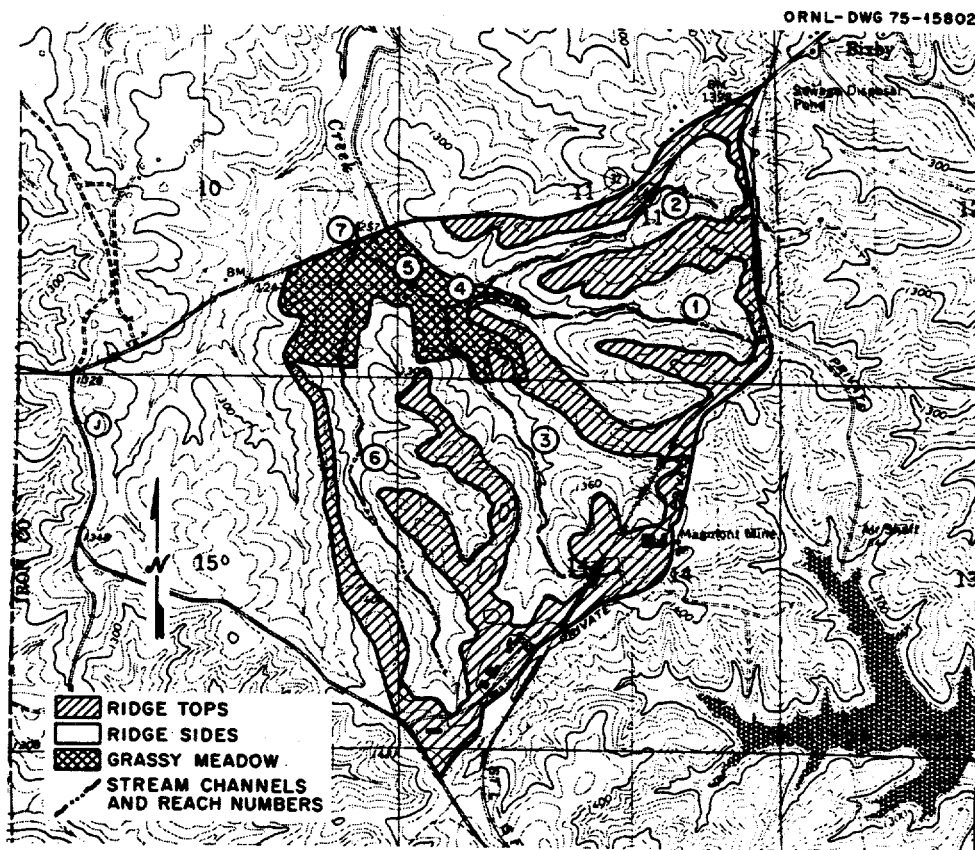


Figure 3.10 The configuration of land segments and channel reaches in Crooked Creek Watershed.

The complicated shapes of the new segments introduce more complexity in determining the average deposition rates to each segment from the sources located at the AMAX smelter. A procedure for area-weighting of deposition rates for a grid of receptor points located throughout the watershed is used to determine the input deposition rates. This grid can be used to study the deposition patterns of the toxicants coming from the various sources at the AMAX smelter. The main sources of the heavy metals are the stack emissions and vehicular suspension of the slag from the ore smelting, which gets spread about on the smelter roads. Figure 3.11 shows the

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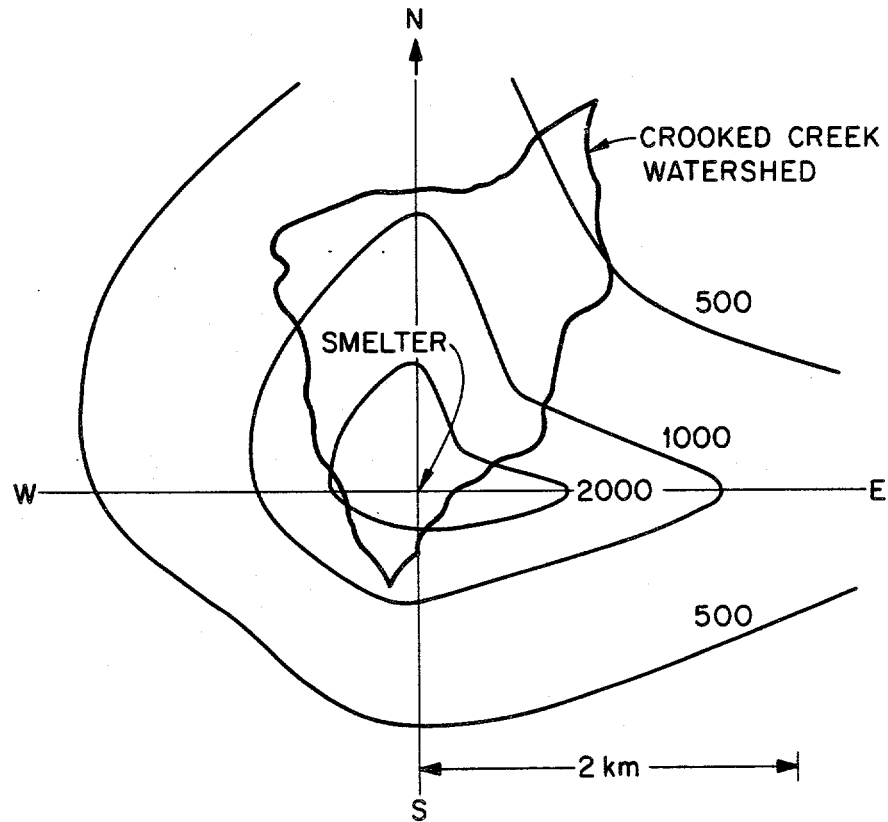


Figure 3.11 Lead deposition rates ( $\text{mg}/\text{m}^2/\text{mo}$ ) for the Crooked Creek Watershed in Missouri.

simulated deposition rates for lead near the Crooked Creek Watershed, using five-year averaged seasonal wind rose data for St. Louis (located 150 km NE of the watershed), and a deposition velocity of 10 cm/sec.

The average monthly deposition rate for lead along a northwest transect from the smelter through the watershed is shown in Figure 3.12. The upper curve shows the deposition rate if a deposition velocity of 10 cm/sec is used; the lower curve shows the rate if the deposition velocity is assumed to be 1 cm/sec. These two deposition velocities correspond to the upper and lower limits, respectively,

expected for the size particles originating from the sources. Data points measured by A. P. Watson<sup>43</sup> for the lead content of the forest floor litter, averaged over the period during which the smelter has operated (six years), have been superimposed on these curves. The error bars indicate maximum and minimum rates based on one standard

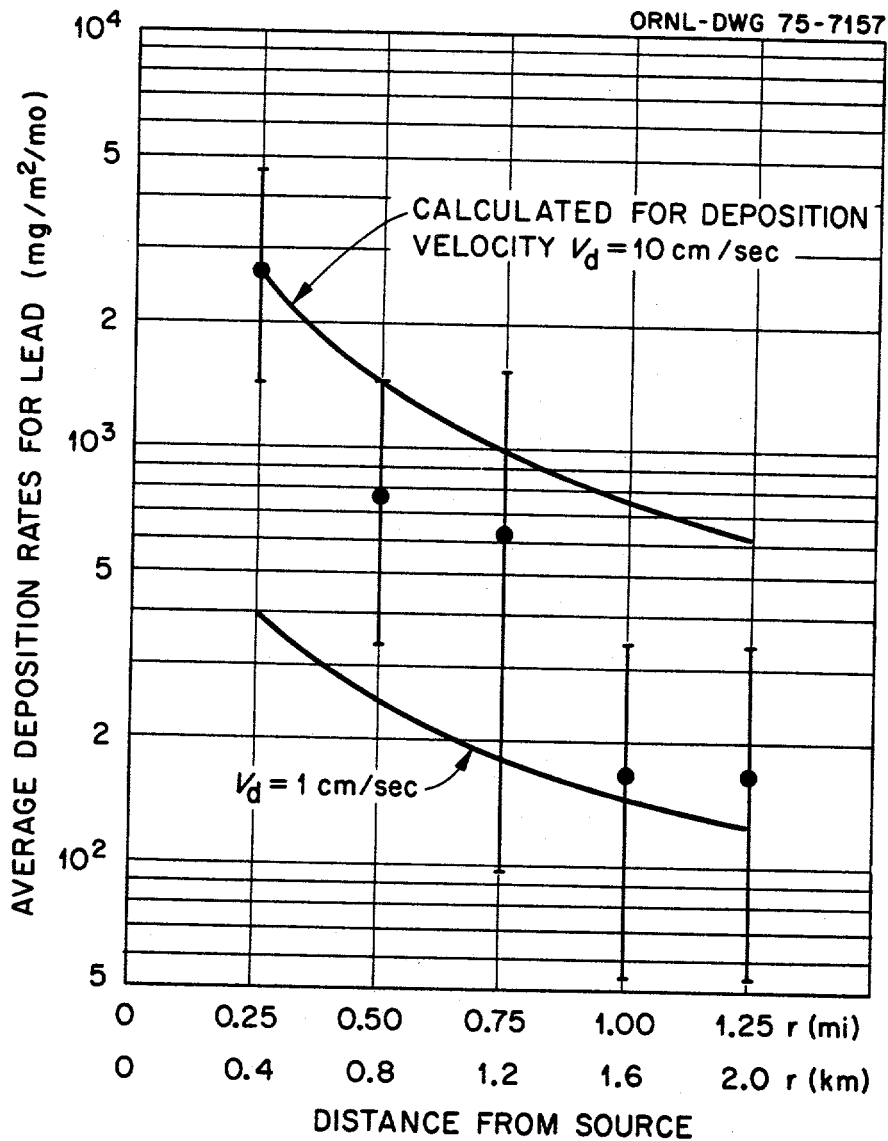


Figure 3.12 Average monthly deposition rate along a northwest transect through Crooked Creek Watershed.



deviation of the experimental data. The data are bracketed by the range of deposition velocity assumed, but more detailed information about the shape of the curve is needed to determine if the effective suspension height of the area source or the particle size should be increased in the model.

Simulations of the hydrologic transport of Pb, Cd, Zn, and Cu with the WHTM have been performed for water year 1974 (WY 74), i.e., October 1, 1973 to September 30, 1974<sup>44</sup>. Stream flows and heavy metal concentrations in outfall at the watershed are compared to the simulated values in Table 3.4 for the storm events studied by J. C. Jennett of the UMR project. Figure 3.13 shows the observed and simulated hydrographs for the storm of September 11, 1974, and illustrates the accuracy of the hydrologic portion of model results. The comparison for heavy metal transport, given in Table 3.4, shows

Table 3.4. Comparison of simulated and measured stream flows and heavy metal concentrations for several storms at Crooked Creek Watershed, New Lead Belt, Mo.

Heavy Metal	Storm Dates	Daily Flows		Simulated Total Metal Transported Per Day [kg]	Daily Average Metal Concentration (unfiltered samples)	
		Measured [cfs]	Simulated [cfs]		Measured [mg/l]	Simulated [mg/l]
Pb	8-18-74	1.69	3.15	8.4	3.7	1.1
	8-29-74	6.75	10.7	1.7	9.0	0.1
	9-11-74	12.7	11.8	16.6	9.9	0.6
Cd	8-28-74	1.69	3.15	8.8	1.8	1.1
	8-29-74	6.75	10.7	16.2	2.8	0.6
	9-11-74	12.7	11.8	26.4	0.57	0.9
Zn	8-28-74	1.69	3.15	11.3	4.57	1.5
	8-29-74	6.75	10.7	5.6	10.01	0.2
	9-11-74	12.7	11.8	41.2	5.43	1.4
Cu	8-28-74	1.69	3.68	2.6	0.18	0.3
	8-29-74	6.75	10.9	5.1	0.50	0.2
	9-11-74	12.7	12.8	13.	0.55	0.4

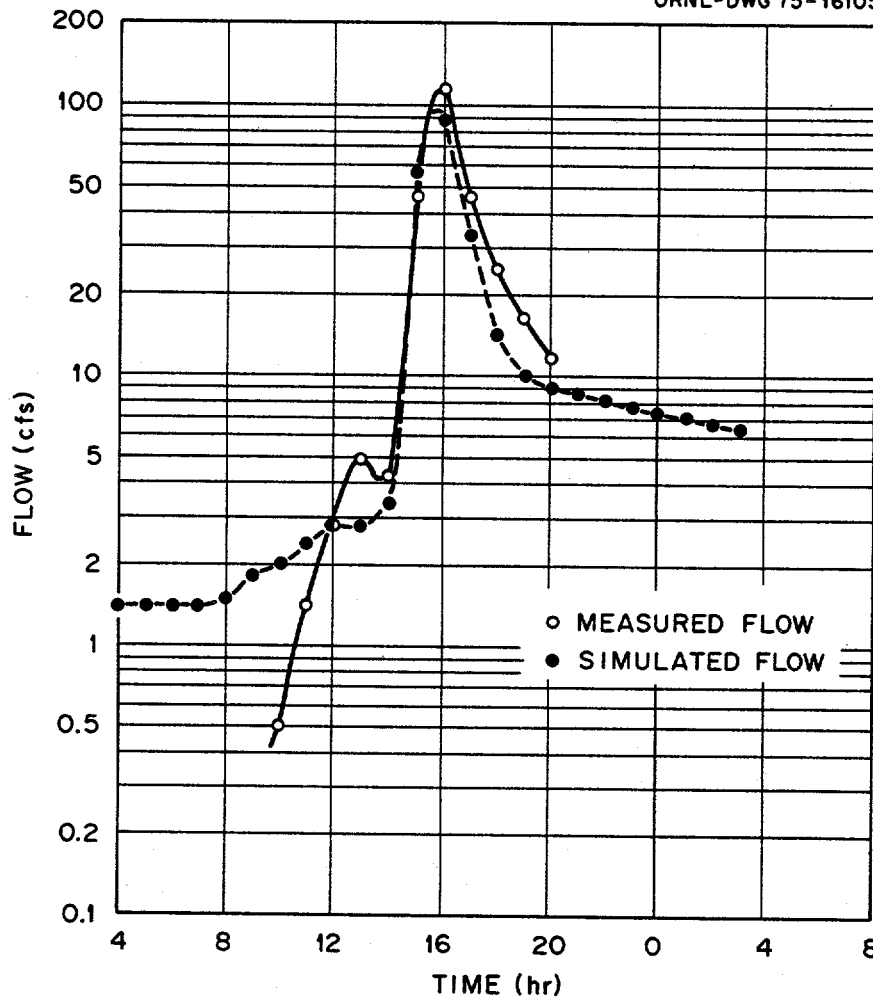


Figure 3.13 Observed and simulated storm hydrographs for Crooked Creek Watershed.

agreement that is generally well within one order of magnitude. The best results were obtained for Cd, Cu, and Zn, which have chemistries that are most nearly represented by the current model assumptions. Our results are consistent with those obtained using SCEHM<sup>11</sup>, as described below, and indicate the need for further studies on the mobility of Pb.

The soil chemistry model SCEHM has been used to simulate the transport of lead, cadmium, zinc, and copper through the soil profile

at a ridge top site on the Crooked Creek Watershed, 1/4 mile from the lead smelter. Atmospheric deposition rates used in the simulation were those found by the New Lead Belt Team<sup>45</sup>. Leaching through litter was simulated using experimentally determined solubilities of heavy metals in highly contaminated litter from Crooked Creek Watershed. Distribution coefficients ( $K_d$ ), which describe the partitioning of heavy metals between soil and soil solution, were experimentally determined for the A1 and A2 soil horizons. Results from a six-year simulation are compared with experimental results in Table 3.5. Because SCEHM does not differentiate between complexed and free heavy metals, agreement is best for those heavy metals, such as zinc and cadmium, which tend to remain as free cations in the soil solution. Copper, however, complexes readily. The complexed form moves through the soil more rapidly, resulting in low experimental values. Calculated results for lead are low, indicating that lead is possibly percolating into the soil in the form of highly insoluble, particulate, lead sulfide.

Table 3.5. Experimental and predicted amounts of exchangeable heavy metals in soils at Crooked Creek Watershed. Values represent conditions after six years of mine and smelter operation.

Metal	Exchangeable amounts (ppm)			
	A1		A2	
	Experimental	Predicted by SCEHM	Experimental	Predicted by SCEHM
Lead	650.0	480.0	180.0	5.6
Cadmium	8.0	5.3	3.8	2.1
Zinc	56.0	53.0	28.0	27.0
Copper	13.0	40.0	5.5	7.8

3.3.2 Application of the UTM to Walker Branch Watershed. The Walker Branch Watershed (WBW), a forested ecosystem located on the ERDA Oak Ridge Reservation, is ideal for our studies because of the extensive documentation and calibration of geology, hydrology, meteorology, and vegetative cover that have been accomplished over the past six years through both ERDA and NSF/IBP Programs. ATM simulations of transport of trace metals and further WHTM simulations of Cd discharge have been the primary focus of our WBW study during the past year. In addition, the code OPTRM has determined a more optimal set of hydrologic parameters valid for WBW.

The Atmospheric Transport Model (ATM) has been used to estimate the deposition and air concentration of trace metals present at Walker Branch Watershed. Much of each metal present comes from the coal burned at three nearby steam plants. The annual coal consumptions at TVA's Kingston and Bull Run plants, and ERDA's Y-12 plant, are  $4 \times 10^6$ ,  $2.5 \times 10^6$ , and  $0.15 \times 10^6$  tons, respectively. It was assumed that 10% of each trace metal present in the coal is emitted from the stacks at Kingston and Y-12, and 15% is emitted at Bull Run. An approximate range of trace metals present in coal was taken from the Allen Steam Plant study<sup>46</sup> and Illinois Geological Survey<sup>47</sup> studies. Calculations were made for three aerosol particle sizes and two types of ground cover (different deposition velocities). For all conditions the calculated wet deposition rates are considerably lower than the dry rates. The computed total depositions for eight elements are listed in Table 3.6, together with the range of

deposition measured in rainfall. There is an overlap in all cases, although the computed values are lower than the maximum values measured, except for Zn.

A more direct comparison can be made for air concentrations, since measurements were made on eighteen elements during July 1974 and February 1975 using two different samplers. The data for seven elements are given in Table 3.7. Again there is an overlap for some elements, indicating that the steam plants are a probable source for

Table 3.6. Comparison of measured and computed trace element deposition on Walker Branch Watershed.

Element	Deposition (grams/ha/month)	
	Measured (in rainfall)	Max. computed
Cd	1.7-31	3.3
Cr	0.5-11	7
Cu	5.6-52	7.6
Hg	0.04-1.2	0.13
Mn	3.8-58	30
Ni	0.9-20	11
Pb	6.7-50	26
Zn	17-72	320

Table 3.7. Comparison of measured and computed monthly air concentrations at Walker Branch Watershed

Element	Air concentration (ng/m <sup>3</sup> )			Overlap?
	Calc. range	Measured		
	7-72 and 7-73	7-74 <sup>a</sup>	2-75 <sup>b</sup>	
Cd	0.03-0.54	4.1	<8	No
Cr	0.9-3.9	1.7	1.8	Yes
Cu	0.5-3.2	8.2	<5	No (close)
Hg	0.008-0.04	0.13	0.15	No
Mn	2.1-10.6	14	7.2	Yes
Pb	0.3-7.6	90	-	No
Zn	3-60	23.4	17.2	Yes

<sup>a</sup>Hi-Vol sampler with Whatman filter.

<sup>b</sup>Andersen pump with Nuclepore filter.

these trace metals. Additional elements for which the computed concentrations were within the measured ranges were Al, As, Ca, Co, K, Na, Ti, and V (see Section 4.3.2 this report). Additional elements which were outside the range were Br, Fe, and Se. Only for Fe was the computed concentration higher than the measured values.

Simulations of the discharge of cadmium from Walker Branch Watershed using the WHTM, as described in last year's progress report<sup>10</sup>, have been expanded to include a 15-month period from June 1973 through August 1974. In the process, it was discovered that some of the experimental data previously reported<sup>48</sup> for Cd streamflow values were in error; these have been corrected. The hydrologic simulation for this time period is shown in Figure 3.14. The para-

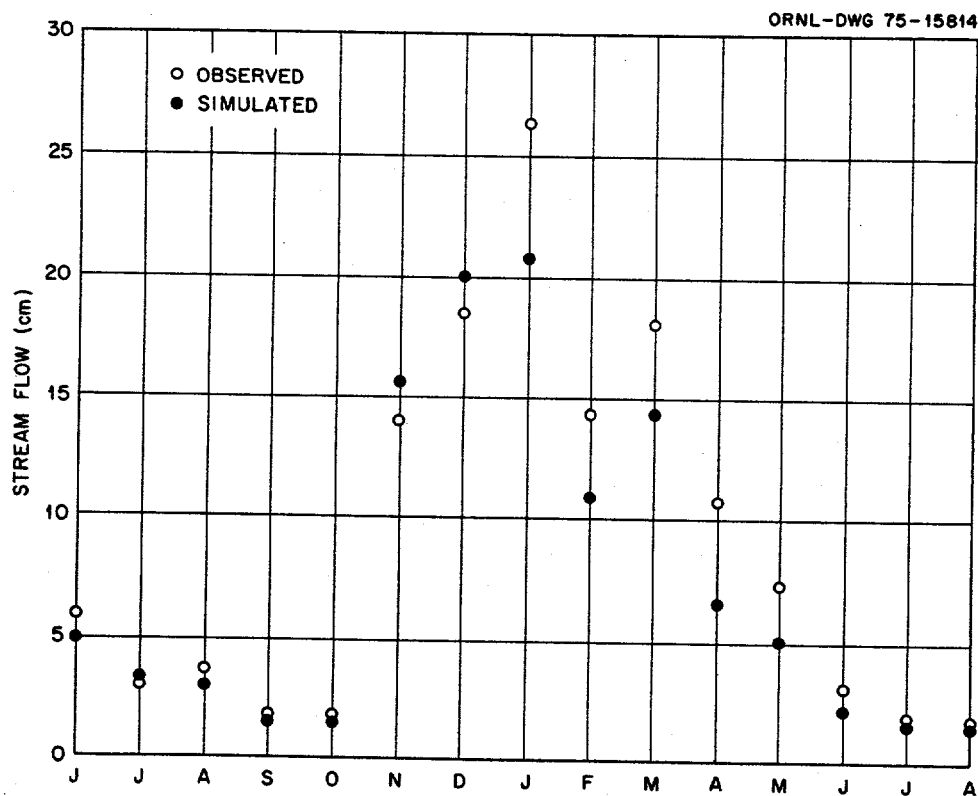


Figure 3.14 Observed and simulated monthly streamflow at Walker Branch Watershed June 1973 - August 1974.

meters are the same as those used in the four-year simulation discussed last year. The simulation is excellent for the summer months but tends to underestimate the higher winter and spring flows. This was a particularly wet winter; the January 1974 streamflow was the highest monthly value recorded since the weirs were installed in 1969. The corresponding Cd simulation is shown in Figure 3.15. The agreement between simulated and observed values is quite good, considering that these represent a retention of Cd by the watershed of greater than 63% (see Table 4.14).

The application of the Optimizing Transport Model to streamflow at Walker Branch Watershed has been described in a previous report<sup>39</sup>. We have since applied the generalized version of this code to determine

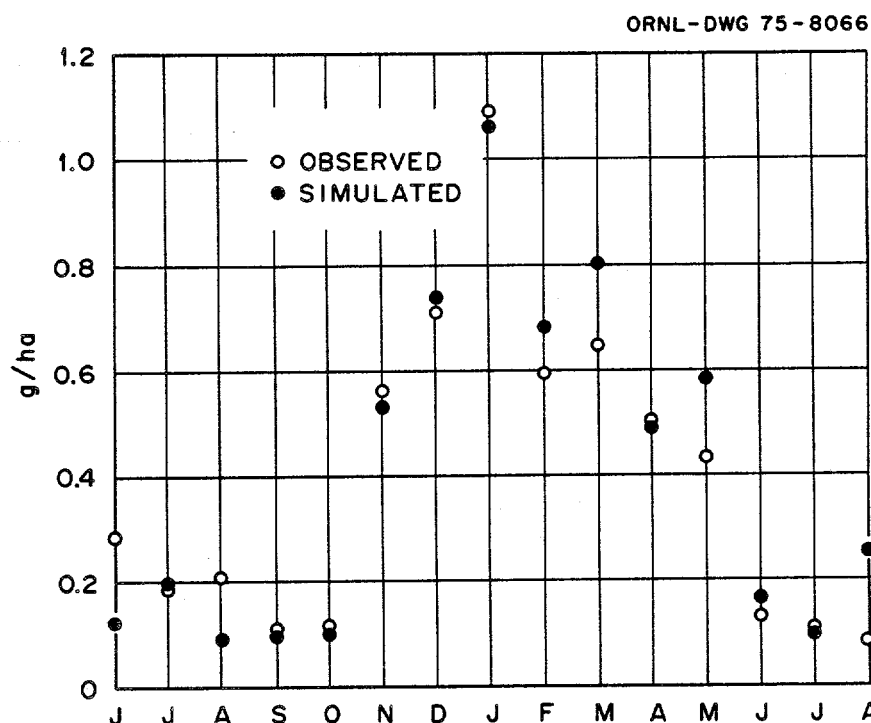


Figure 3.15 Observed and simulated monthly cadmium export in streamflow at Walker Branch Watershed June 1973 - August 1974.

parameters for the simulation of potassium transport on Walker Branch Watershed. Fig. 3.16 shows the results of this application to the east fork of Walker Branch. In this figure, we compare measured monthly values with the simulated monthly potassium transport

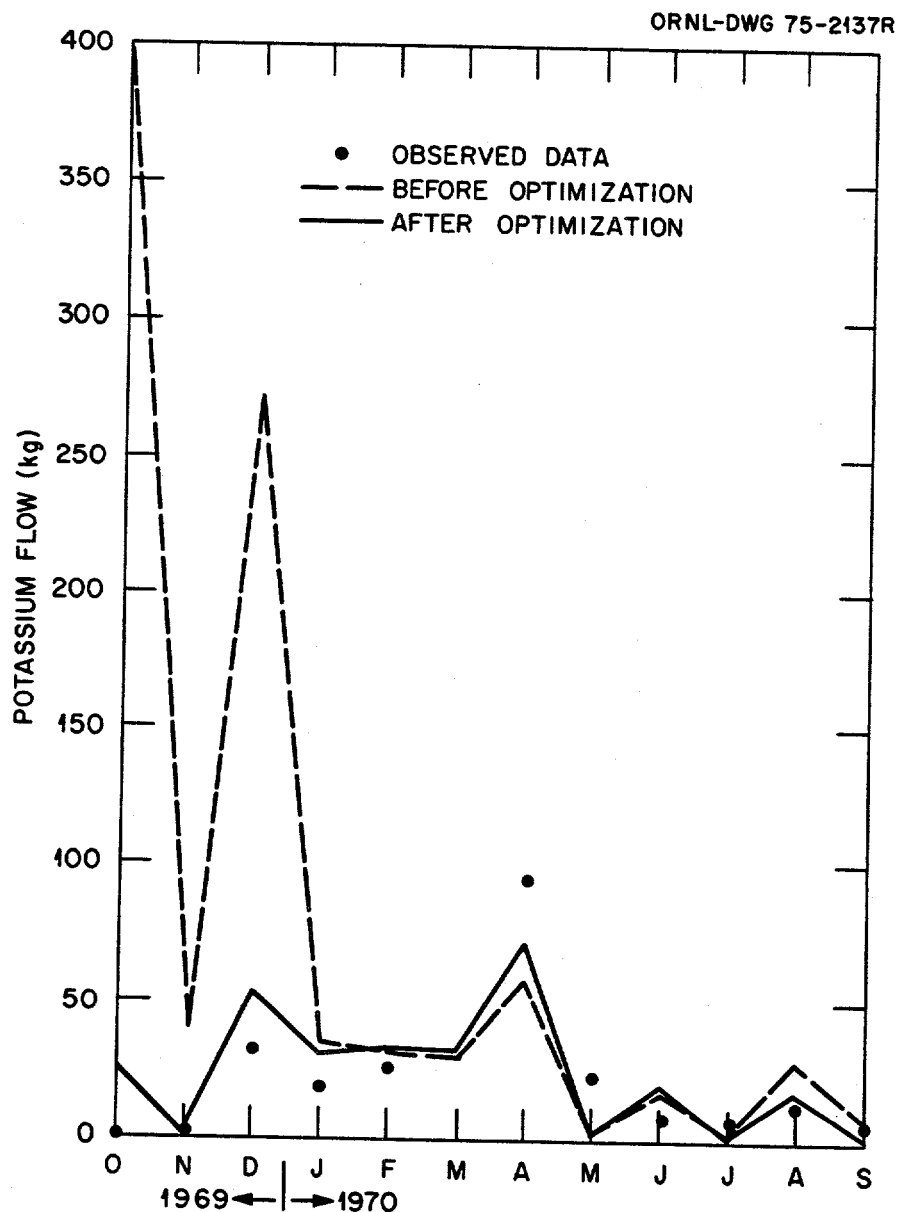


Figure 3.16 Simulated monthly potassium transport before and after optimization, compared to observations.



in water year 1970 both before and after parameter set optimization. The simulation following the parameter set optimization agrees much more closely to the observed values than does the simulation using our initial parameter estimates. Parameters determined in this optimization run were FF and KD. FF is a sensitive determinant of the simulated rate of soil erosion at the land surface as driven by raindrop impaction and sheet hydraulic flow. KD is the chemical exchange coefficient expressing the partitioning of potassium between the soil particles and water. It is defined as

$$KD = \frac{\text{grams of adsorbed contaminant per gram of soil}}{\text{grams of dissolved contaminant per milliliter of water}}$$

Table 3.8 gives the range, initial value, and final value of these parameters and of F, the residual function defined in Section 3.2.4 of this report. Also shown in this table are the initial and final simulated yearly potassium transport and the observed yearly potassium transport value. In one execution of OPTRM, the residual function

Table 3.8. Initial and final transport-related parameter values that were used in optimization

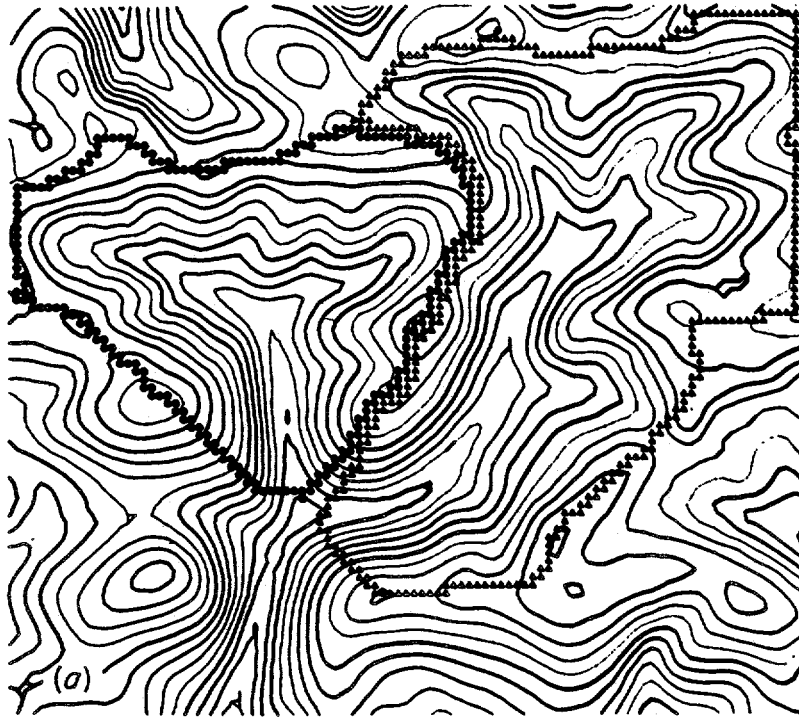
Parameter	Definition	Range		Initial value	Final value
		min	max		
FF	Empirical erosion parameter	0.5	300.0	100.0	294.8
KD	Chemical exchange coefficient	1.0	100.0	4.0	68.58
F	Residual, CFSD basis			$0.219 \cdot 10^6$	$0.343 \cdot 10^4$
Yearly simulated potassium transport (Kg)				925.0	303.0
Yearly observed potassium transport (Kg)					301.0 <sup>a</sup>

<sup>a</sup>See Ref. 49.

decreased by approximately two orders of magnitude with an attendant enhanced agreement between observed and simulated potassium transport. Values of parameters other than FF and KD were not varied during the course of this simulation. These were either estimated or measured or, in the case of the six parameters discussed previously<sup>39</sup>, determined using OPTRM prior to this simulation. Note that we have achieved a significant improvement in simulation results through optimizing a parameter set of only two transport parameters. This indicates the importance in choosing those parameters most closely related to the process being investigated.

The digital topography code described in Section 3.2.5 has been used to determine basin divides and flow directions for Walker Branch Watershed. The topographic divides found by the code are shown in Fig. 3.17a, and the flow directions are shown in Fig. 3.17b. For the west branch of the Walker Branch Watershed, the code calculated an area of 102 acres with average slope of 22.3%; for the east branch, 163 acres and 21.2%. We consider these values reasonably close to the 95 and 146 acres determined using a planimeter on a contour map with visually estimated boundaries. The differences could arise from the lack of information near the watershed boundaries, overall scaling errors in the grid increment, or in the somewhat subjective choice of the boundaries used in planimetry.

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ORNL DWG. 75-13443

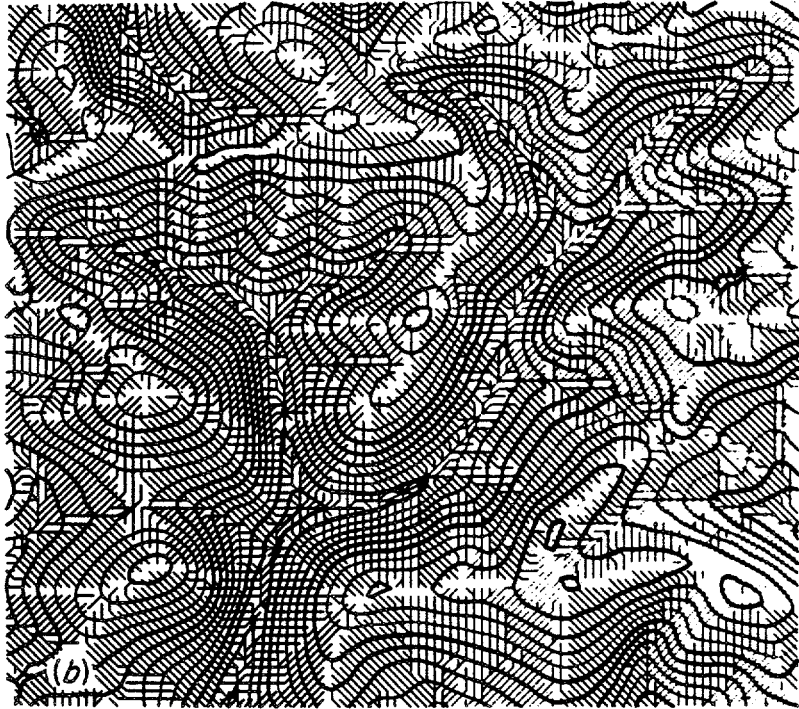


Figure 3.17 (a) Computer-determined divides of the east and west forks of Walker Branch Watershed; (b) Computed flow directions superimposed on contour lines in Walker Branch Watershed.

### 3.4 References

1. M. T. Mills and M. Reeves, A Multi-Source Atmospheric Transport Model for Deposition of Trace Contaminants, ORNL-NSF-EATC-2, Oak Ridge National Laboratory, (1973).
2. W. M. Culkowski and M. R. Patterson, A Comprehensive Atmospheric Transport and Diffusion Model, ORNL-NSF-EATC-17, Oak Ridge National Laboratory, (1975).
3. Thomas W. Horst, "A Surface-Depletion Model for Deposition from a Gaussian Plume", Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants - 1974 Symposium, Sept. 4-6, 1974, Battelle Pacific Northwest Laboratories, Richland, Washington.
4. A. W. Castelman, Jr., R. E. Davis, H. R. Munkelwitz, I. N. Tang, and William P. Wood, "Kinetics of Association Reactions Pertaining to  $H_2SO_4$  Aerosol Formation", in International J. of Chemical Kinetics, Chem. Kinetics Symposium No. 1, S. W. Benson, D. N. Golden, and J. R. Baker, Eds., Interscience, New York, 1975, p. 543.
5. C. F. Baes, J. T. Holdeman, and W. M. Culkowski, SULCAL: A Model of Sulfur Chemistry in a Plume, ORNL-NSF-EATC-21 (in preparation), (1975).
6. J. T. Holdeman, C. F. Baes, C. L. Begovich, and W. M. Culkowski, Incorporation of the Sulfur Chemistry Model SULCAL into the Atmospheric Transport Model (in preparation), (1975).
7. M. R. Patterson, J. K. Munro, D. E. Fields, R. D. Ellison, A. A. Brooks, and D. D. Huff, A User's Manual for the FORTRAN IV Version of the Wisconsin Hydrologic Transport Model, ORNL-NSF-EATC-7, EDFB-IBP-74-9, (1974).
8. J. J. Jurinak, S. H. Lai, and J. J. Hassett, Cation Transport in Soils and Factors Affecting Soil Carbonate Solubility, EPA-R2-73-235, Utah State University, (May 1973).
9. G. R. Dutt, M. J. Shaffer, and W. J. Moore, Computer Simulation Model of Dynamic Bio-Physiochemical Processes in Soils, Technical Bulletin 196, University of Arizona, (October 1972).
10. M. R. Patterson, et al., "Development of a Unified Transport Model", in Ecology and Analysis of Trace Contaminants Progress Report, October 1973 - September 1974, W. Fulkerson, W. D. Shults, and R. I. Van Hook (eds.), ORNL-NSF-EATC-11, Oak Ridge National Laboratory, (December 1974).

11. C. L. Begovich and D. R. Jackson, Documentation and Application of SCEHM: A Model for Soil Chemical Exchange of Heavy Metals, ORNL-NSF-EATC-16, Oak Ridge National Laboratory, (1975).
12. N. M. Larson and M. Reeves, Analytical Analysis of Soil Moisture and Trace Contaminant Transport, ORNL-NSF-EATC-12, Oak Ridge National Laboratory, (1975).
13. R. P. Betson and J. B. Marius, "Source Areas of Storm Runoff", Water Resour. Res. 5(3), (Nov. 1969).
14. W. T. Dickinson and H. Whiteley, "Watershed Areas Contributing to Runoff", in Symposium on Results of Research on Representative and Experimental Basins. Intern. Assoc. of Sci. Hydrol. Publ. 96, pp. 1.12-1.26, (1970).
15. Edwin T. Engman and Andrew S. Rogowski, "A Partial Areas Model for Storm Flow Synthesis", Water Resour. Res. 10(3): 464-472, (1974).
16. R. A. Freeze, "Role of Subsurface Flow in Generating Surface Runoff. 2. Upstream Source Areas", Water Resour. Res. 8(5): 1272-1283, (1972).
17. W. J. Gburek and W. R. Heald, "Soluble Phosphate Output of an Agricultural Watershed in Pennsylvania", Water Resour. Res. 10(1): 113-118, (1974).
18. J. D. Hewlett, "Watershed Management", in Annual Report for 1961, Southeastern Forest Experiment Station, U.S. Forest Service, pp. 61-66, (1961).
19. A. M. Ishaq, "Application of Remote Sensing to the Location of Hydrologically Active (Source) Areas", Ph.D. Dissertation, Civil and Environmental Engineering Dept., University of Wisconsin (Msn), 208 p., (1974).
20. M. T. Lee and J. W. Delleur, "Analysis of Geomorphologic Data and a Dynamic Contributing Area Model for Runoff Estimation", Water Resources Research Centre Tech. Rep. 24. Purdue University, Lafayette, Indiana, (Sept. 1972).
21. K. R. Dixon, R. J. Luxmoore, and C. L. Begovich, CERES - A Model of Hourly Forest Stand Growth in Relation to Water Stress and Translocation (in preparation), (1975).
22. R. J. Luxmoore, K. R. Dixon, and C. L. Begovich, DRYADS - A Model of Solute Transport in Forest Stands (in preparation), (1975).

23. J. H. M. Thornley, "A Model to Describe the Partitioning of Photosynthate during Vegetative Plant Growth". Ann. Bot. 33: 419-430. (1972).
24. H. L. Penman and R. K. Schofield, "Some Physical Aspects of Assimilation and Transpiration", pp. 115-129 in Carbon Dioxide Fixation and Photosynthesis, Symp. Soc. Exp. Biol. No. 5. Acad. Press, N.Y., (1951).
25. P. Gaestra, Photosynthesis of Crop Plants as Influenced by Light, Carbon Dioxide, Temperature, and Stomatal Diffusion Resistance. Meded. Landouwhogesch. Wageningen 59: 1-68, (1959).
26. J. S. Boyer, "Leaf Enlargement and Metabolic Rates in Corn, Soybean, and Sunflowers at Various Leaf Water Potentials", Plant Physiology, Volume 46, pp. 233-235, (1970).
27. J. P. Baldwin, P. H. Nye, and P. B. Tinker, "Uptake of Solutes by Multiple Root Systems from Soil, III. A Model for Calculating the Solute Uptake by a Randomly Dispersed Root System Developing in a Finite Volume of Soil". Plant and Soil, Volume 38, pp. 621-635, (1975).
28. D. E. Fields, A Numerical Simulation of Water-Borne Sediment Transport, Paper presented at ACM Regional Conference, Nashville, Tennessee, (April 1974).
29. D. E. Fields, A Model of Sediment-Associated Trace Contaminant Transport, Paper presented at the Second Annual NSF-RANN Trace Contaminants Conference, Asilomar, California, (August 1974).
30. D. E. Fields, A Simulation of Trace Contaminant Transport through a Channel System with Chemical Exchange between Sediment and Water, Paper presented at Fall Annual Meeting of American Geophysical Union, San Francisco, California, (December 1974).
31. J. R. L. Allen, Current Ripples: Their Relation to Patterns of Water and Sediment Motion, North Holland Publishing Company, (1968).
32. W. M. Twenhoffel, Principles of Sedimentation, Second Edition, McGraw-Hill Book Company, Inc., (1950).
33. A. Hazen, "On Sedimentation", Trans. Am. Soc. Civil Engineers 53, (1914).
34. D. E. Fields and R. J. Raridon, "Computer Simulation of Mass Transport on Walker Branch Watershed, Oak Ridge, Tennessee. Part I. Water and Sediment Transport", Paper presented at the Tennessee Academy of Science, Memphis, Tennessee, (November 1974).

35. R. J. Raridon and D. E. Fields, "Computer Simulation of Mass Transport on Walker Branch Watershed, Oak Ridge, Tennessee. Part II. Trace Element Transport", Paper presented at the Tennessee Academy of Science, Memphis, Tennessee, (November 1974).
36. D. E. Fields, CHNSED: Simulation of Sediment and Trace Contaminant Transport with Sediment/Contaminant Interaction, ORNL-NSF-EATC-19, Oak Ridge National Laboratory, (1975).
37. R. A. Bagnold, "An Approach to the Sediment Transport Problem from General Physics", Geological Survey Professional Paper 422-1, U.S. Government Printing Office, (1966).
38. F. B. Toffaleti, "A Procedure for Computation of the Total River Sand Discharge and Detailed Distribution, Bed to Surface", Technical Report #5, Committee on Channel Stabilization, U.S. Army Corps of Engineers, (November 1968).
39. M. R. Patterson, et al., "Development of a Unified Transport Model for Toxic Materials", in Ecology and Analysis of Trace Contaminants Progress Report, January 1973 - September 1973, W. Fulkerson, W. D. Shults, and R. I. Van Hook (eds.), ORNL-NSF-EATC-6, Oak Ridge National Laboratory, (January 1974).
40. D. E. Fields and S. B. Watson, OPTRM - A Hydrologic Transport Model with Parameter Optimization, ORNL-NSF-EATC-14, Oak Ridge National Laboratory, (September 1975).
41. T. C. Tucker and D. E. Fields, Digital Topography; Calculation of Watershed Areas and Slope, Oak Ridge National Laboratory Report ORNL-NSF-EATC-20, (1975).
42. R. L. Jones, A Generalized Digital Contouring Program, NSA TN D-6022, Langley Research Center, Hampton, Virginia, (January 1971).
43. A. P. Watson, Private Communication.
44. J. K. Munro, et al., Application of the Unified Transport Model to Crooked Creek Watershed (in preparation), (1976).
45. B. G. Wixson and J. C. Jennett (eds.), An Interdisciplinary Investigation of Environmental Pollution by Lead and Other Heavy Metals from Industrial Development in the New Lead Belt of South-eastern Missouri, Interim Progress Report, May 1972 to June 1974, University of Missouri, Rolla, report to National Science Foundation, (June 1974).

46. D. H. Klein, et al., Pathways of Thirty-eight Trace Elements Through a Coal-Fired Power Plant, Oak Ridge National Laboratory (submitted for publication), (1975).
47. R. R. Ruch, H. J. Gluskoter, and W. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: A Final Report", Environmental Geology Notes, No. 72, (August 1974).
48. R. J. Raridon, D. E. Fields, G. S. Henderson, and A. W. Andren, "Transport of Potassium and Cadmium on Walker Branch Watershed", Proceedings of the Second Annual NSF Trace Contaminants Conference, Asilomar, California, pp. 210-215, LBL-3217, (1975).
49. J. W. Elwood and G. S. Henderson, Hydrologic and Chemical Budgets at Oak Ridge, Tennessee, IBP-EDFB-73-15, Oak Ridge National Laboratory, (1973).



#### 4. ECOLOGICAL RESEARCH

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##### 4.1 Introduction

The Ecological Research Section of the EATC Program is composed of three major research areas: Holston River-Cherokee Reservoir Studies, Walker Branch Watershed Studies, and Crooked Creek Watershed Studies. The scientific leaders for each of these areas are, respectively, S. G. Hildebrand, S. E. Lindberg, and D. R. Jackson. Research activities in the Holston River-Cherokee Reservoir System have been focused on determining the biogeochemical cycling and transport of mercury released from the waste disposal areas of a defunct chloro-alkali plant in Saltville, Virginia. Walker Branch Watershed Studies have been designed to identify and evaluate the atmospheric input and hydrologic output of coal-fired power plant derived trace elements deposited on the forested landscape. Crooked Creek Watershed Studies have been concerned with physical and biological transport of Cd, Pb, Cu, and Zn emitted from a lead smelter in southeastern Missouri. Our work in Crooked Creek has also lead to the identification of several ecosystem level effects of these trace elements.

Successful attainment of our research objectives in these three study sites has depended strongly upon the development of analytical measurement techniques for determinations of elemental concentrations and chemical speciation in a variety of environmental samples (see

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<sup>a</sup>Task Leader.

Section 5). Application of the Unified Transport Model (Section 3.3) to both Walker Branch and Crooked Creek Watersheds has depended upon accurate determination of parameters describing the movement of trace elements through these landscapes. One of our objectives in the Ecological Research area has been to provide these parameter estimates - as well as to participate in the development and modification of transport models depicting elemental flows through soils, soil water, and vegetation.

The primary objectives of the Ecological Research area include 1) development of techniques for evaluating trace element transport through ecosystems, 2) application of these techniques to areas contaminated by industrial emissions, and 3) incorporation of this information into the development of mechanistic ecological models for incorporation into the Unified Transport Model. In the following sections, we present our technical accomplishments for the period since our previous report.<sup>1</sup>

## 4.2 Holston River - Cherokee Reservoir Studies

4.2.1 Introduction and Methods. The North Fork of the Holston River (NFHR) originates in southwest Virginia, flows southwest into Tennessee, and after confluence with the South Fork, forms the main Holston River. The Holston River was impounded in 1942 forming Cherokee Reservoir (Fig. 4.1). A chlor-alkali plant located on the North Fork Holston River at Saltville, Virginia (approximately 277 km upstream from Cherokee Dam) in the 1950's began using a mercury cathode in the electrolytic separation of sodium chloride.<sup>2</sup> Salt wastes from the manufacturing process have been deposited in two waste disposal ponds of approximately 120 acres (49 ha.) adjacent to the river. Mercury contamination in the North

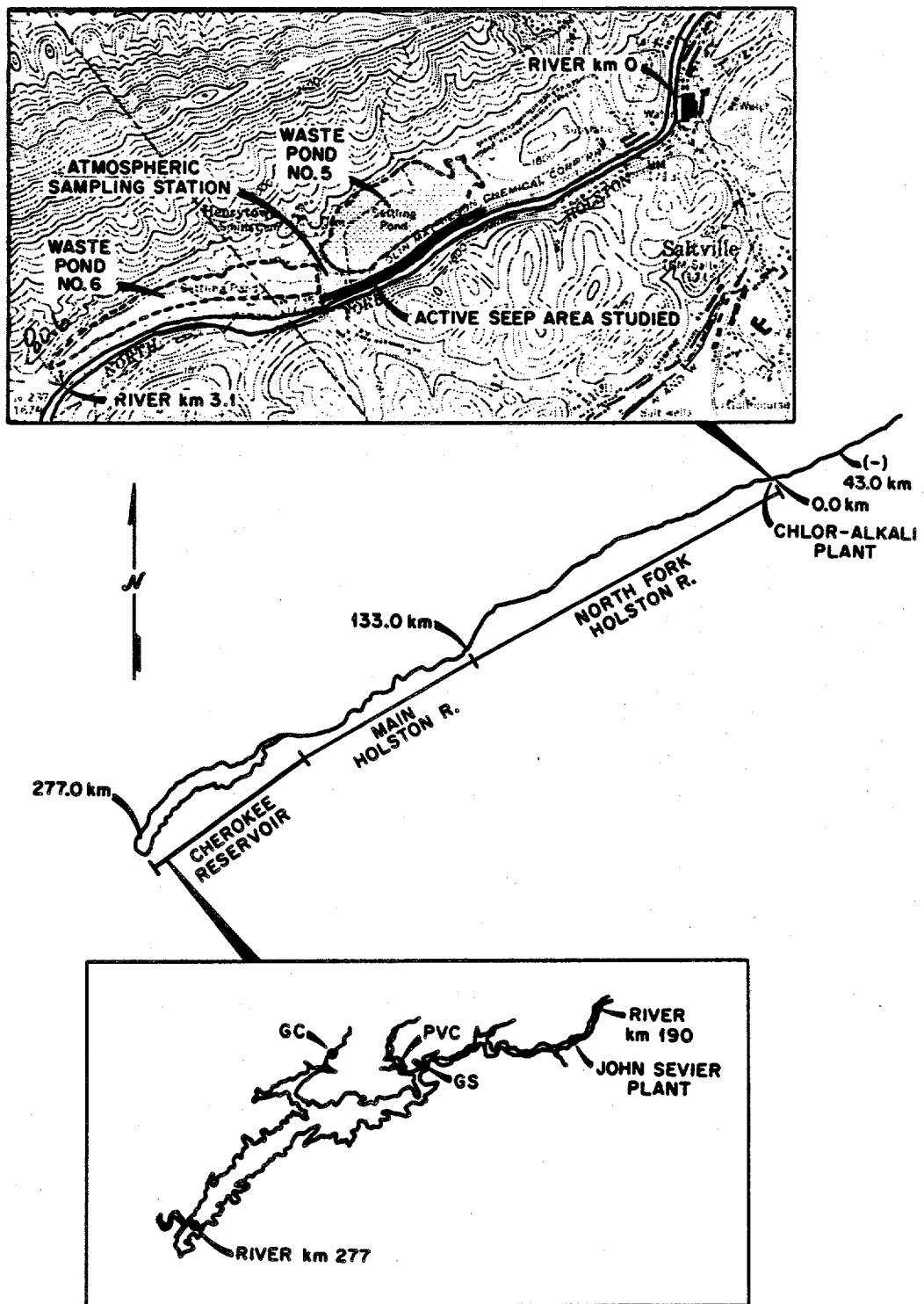


Figure 4.1 Schematic of Holston-Cherokee System with detailed location of waste disposal ponds and sediment core stations in Cherokee Reservoir. GC = German Creek, PVC = Poor Valley Creek, GS = Galbraith Springs.

Fork was observed in 1970 and subsequent investigations have verified the extent of contamination.<sup>2-6</sup>

The chlor-alkali plant was closed down in 1972 due to the high cost of complying with existing water quality standards for chlorides, total dissolved solids and mercury.<sup>2</sup> Our observations indicate that the plant waste disposal ponds are a continuing source of mercury contamination in the North Fork.<sup>3</sup>

The overall objective of our research on the Holston-Cherokee system is to increase our understanding of the biogeochemical cycling and transport of mercury in this contaminated environment. Specific objectives include: 1) determine the distribution of mercury in water, sediments, and biota of the Holston-Cherokee system to provide insight into mechanisms of transport and bioaccumulation; 2) determine the extent of continuing mercury input to the system; and 3) investigate potential atmospheric emissions of mercury from existing waste disposal ponds of the chlor-alkali plant.

In August 1974 and 1975 fish and benthic invertebrates were collected at select stations on the Holston-Cherokee system. Fish were collected by electrofishing and selective poison while benthic invertebrates were collected by disturbing river substrate upstream from a collecting net. Fish and benthic invertebrates were processed and analyzed for total and methylmercury by previously reported methods.<sup>3,7,8</sup>

Water samples were collected in 1975 by standard methods at select stations.<sup>9</sup> Water samples to be analyzed for dissolved and particulate mercury were filtered (0.45  $\mu$ ) within five minutes of collection utilizing a filtration system developed at our Laboratory.<sup>10</sup> Routine

handling of total water samples followed procedures previously described.<sup>3</sup>

Sediment samples in the North Fork Holston River were collected by hand in backwaters or by Ekman dredge depending on water depth. Core samples in Cherokee Reservoir were collected with a modified Livingston corer and samples from the waste disposal ponds were manually taken in polycarbonate or aluminum tubes. Sediment samples were wet sieved (44  $\mu$  or 2 mm standard sieve) and processed as previously reported.<sup>3</sup> The appearance and texture of the samples that were sieved through the 2 mm mesh indicated that they consisted of fine silts and clays (< 44  $\mu$ ) and for our purposes can be considered as such. Water and sediment samples were analyzed for total mercury<sup>7</sup> and supportive chemical data were obtained following the methods in reference 11.

4.2.2 Geochemical Studies of Mercury. Table 4.1 summarizes relevant geochemical data collected during 1975. Stations are identified by river kilometer with the reference point located at the abandoned chlor-alkali plant (see Fig. 4.1 and Table 4.2). Replicate stations are described by identical locations but different sampling dates. The most striking patterns in the distribution of Hg in the system relate to the variations in bottom sediment Hg and total Hg in the water column with river kilometer (Fig. 4.2). The impact of mercury inputs from the waste disposal pond area on the Hg distribution in the NFHR is obvious considering the strong gradient of decreasing Hg concentration with distance downstream. An indication of temporal variability is shown as the range in total Hg concentration in the water for

Table 4.1. Distribution of mercury and other physical-chemical parameters for the Holston-Cherokee System at select stations in 1975.

Stations are river kilometers above (—) and below plant.

Station (river km)	pH	Specific conductance ( $\mu$ mhos/cm)	Chlorides (mg/l)	Dissolved organic carbon (mg/l)	Particulate organic carbon (mg/l)	Suspended solids (mg/l)	Total Hg water ( $\mu$ g/l)	Dissolved Hg water ( $\mu$ g/l)	Hg on suspended particulates ( $\mu$ g/g dry wt.)	Hg bed sediment ( $\mu$ g/g dry wt.)	Date
-43.0	8.0	248	1.8	2.16	—	12.0	0.070	0.001	5.80	0.136	8/26
-14.0	8.3	253	4.2	1.62	—	11.2	0.025	ND <sup>b</sup>	2.30	0.118	8/26
-9.0	8.1	251	4.2	2.32	—	7.8	0.034	—	—	0.165	8/26
-2.7	8.1	258	5.2	1.94	—	5.2	0.015	—	—	0.114	8/27
-2.7	8.4	— <sup>a</sup>	2.8	—	—	—	0.003	ND	—	—	5/21
-2.7	8.0	246	2.7	3.15	0.58	16.8	0.006	ND	0.36	—	7/29
-2.7	8.2	244	2.5	2.05	0.32	12.0	0.007	ND	0.58	—	7/30
-2.7	8.1	266	2.5	3.31	0.56	12.4	0.008	ND	0.65	—	7/31
3.1	8.2	5150	1490.0	2.71	—	11.2	0.210	0.056	13.70	18.50	8/26
3.1	8.7	448	156.0	—	—	8.9	0.093	0.047	5.30	—	5/21
3.1	8.1	1405	427.0	2.01	0.36	9.8	0.196	0.071	12.90	—	7/29
6.4	8.3	4000	1275.0	2.98	0.92	12.8	0.167	0.075	7.20	—	7/29
6.4	8.0	1280	358.0	3.60	0.30	12.4	0.185	0.050	10.90	—	7/30
6.4	8.1	5700	1848.0	3.05	1.22	14.8	0.193	0.074	5.00	—	7/31
9.7	8.2	1179	300.0	2.36	—	4.2	0.074	0.040	8.10	9.20	8/26
17.0	8.2	1173	300.0	2.12	—	3.0	0.058	0.028	10.00	6.20	8/26
21.0	8.4	1250	334.0	3.83	—	6.2	0.067	0.027	6.40	4.30	8/26
43.0	8.4	821	216.0	2.60	—	4.0	0.032	0.021	1.20	2.40	8/26
133.0	8.1	669	158.0	2.73	—	12.2	0.025	0.018	0.57	0.92	8/27
184.0	7.6	354	43.2	3.28	1.59	4.8	0.010	—	—	—	9/9
190.0	7.7	205	12.6	1.94	1.02	19.8	0.029	0.010	0.96	0.82	9/9
277.0	8.5	224	14.1	1.81	0.70	3.8	0.006	0.005	0.26	—	9/9
277.0	7.7	245	14.0	1.72	0.74	3.8	0.009	0.004	1.30	—	9/10
277.0	7.4	267	15.0	1.86	0.93	21.0	0.012	0.006	0.29	0.48	9/10
278.0	7.5	246	14.3	1.94	0.91	6.4	0.005	—	—	—	9/10

<sup>a</sup>Not measured.

<sup>b</sup>Not detected.

Table 4.2. Location of sampling stations on the Holston-Cherokee System

Station description	Actual river mile	Miles above (-) and below plant	Km above (-) and below plant
North Fork Holston River			
Chatham Hill	109	-26.5	-43.0
Old Broadford	91	-8.5	-14.0
Neil Bridge	88.1	-5.6	-9.0
McCrary	85.9	-3.4	-5.5
USGS Station (0.4 mi below)	84.2	-1.7	-2.7
Chlor-Alkali Plant	82.5	0	0
Transect	80.6	1.9	3.1
Below disposal ponds	81.0	2.3	3.7
Railroad trestle	78.5	4.0	6.4
McKenna Island	76.5	6.0	9.7
Swinging bridge	72.0	10.5	17.0
Hayters Gap	69.5	13.0	21.0
Holston	59.5	23.0	37.0
Hines Island	56.0	26.5	43.0
Mendota	39	43.5	70.0
Hilton	22	60.5	97.0
Kingsport	0	82.5	133.0
Amis	110	114.5	184.0
Cherokee Reservoir			
H.B. Day Bridge	103	121.5	196.0
Malinda	98	126.5	204.0
Fall Creek Dock	81	143.0	230.0
25E Bridge	76	148.0	238.0
Cherokee Dam	52	172.0	277.0

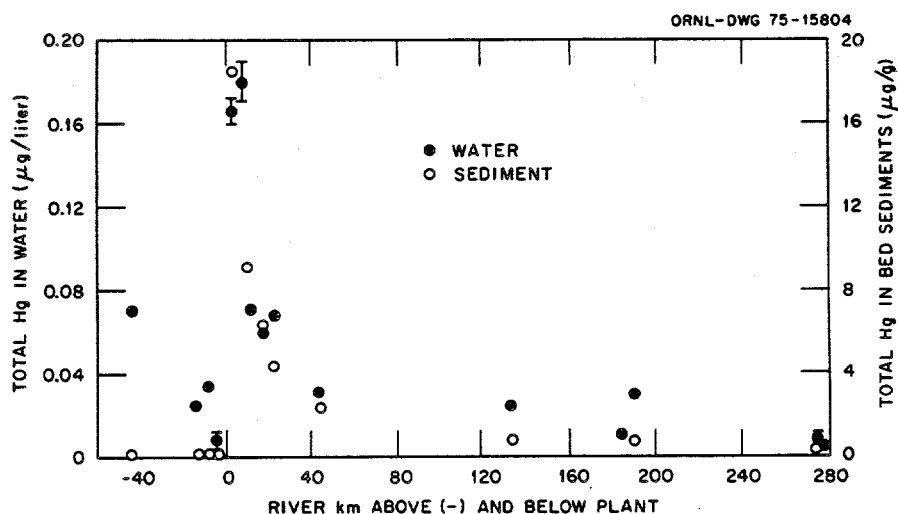


Figure 4.2 Distribution of total mercury in Holston River water (unfiltered) and sediment (dry weight) above and below the chlor-alkali plant in 1975. Error bars = 1 S. D.

three stations near the source area (i.e., stations at -2.7, 3.1, and 6.4 km).

We have hypothesized that the main downstream transport of mercury from the source area in Virginia to Cherokee Reservoir occurs in the particulate phase.<sup>3</sup> If this is indeed the case, one would expect to find elevated concentrations of Hg in fine sediments ( $< 44 \mu$ ) which are deposited where the flow of the Holston is slowed upon entering quiescent waters (e.g., John Sevier Detention Lake and Lake Cherokee). Other factors, such as the source rocks of the sediments, being equal, fine-grained sediment inputs from other, presumably uncontaminated, tributaries such as Poor Valley Creek and German Creek should not show elevated mercury concentrations.

Table 4.3 describes the distribution of total mercury in size fractionated bottom sediments. The three areas involved include one station near the main river channel in the reservoir (Galbraith Springs) and two stations in delta areas of tributaries to the reservoir other than the Holston River itself (Poor Valley Creek and German Creek). These areas are illustrated in Fig. 4.1.

Table 4.3. Mercury concentrations in size fractionated sediments from three tributaries of the Cherokee Reservoir.

Location	Depth (cm)	% $<44 \mu$	$\Sigma$ % OM	$<44 \mu$ % OM	Hg (ppm)		
					$\Sigma$	$<44 \mu$	$>44 \mu$
German Creek <sup>a</sup>	0-5	40	2.7	7.4	0.146	0.290	0.050
	5-10	60	2.8	3.8	0.132	0.171	0.067
Galbraith Springs <sup>b</sup>	0-5	12	1.6	7.3	0.177	1.090	0.043
	5-10	12	1.1	7.4	0.152	0.890	0.052
Poor Valley Creek <sup>c</sup>	0-5	11	2.5	3.1	0.077	0.220	0.053
	5-10	50	3.5	5.1	0.111	0.135	0.061

<sup>a</sup>Station GC in figure 1.

<sup>b</sup>Station GS in figure 1, located in the Holston R tributary.

<sup>c</sup>Station PVC in figure 1.



Although the Hg concentrations in the unfractionated sediment samples are quite similar and do not indicate any disproportionate effect of the Holston River on the Hg burden of the reservoir, the concentrations in the  $< 44 \mu$  fraction in sediments derived from the Holston River are elevated by a factor of 3-8 over the values for sediments derived from the other tributaries. Thus if the concentrations of mercury in similar size fractions, especially the easily transported sizes ( $< 44 \mu$ ) are compared, it is apparent that significant differences exist. The similarity in Hg concentrations in the  $< 44 \mu$  sediment fraction at the Holston tributary station (Galbraith Springs) with the suspended sediments and fine bottom sediments collected at the river station 25 km upstream (station at river km 190, Table 4.2) lends considerable support to the above hypothesis. However, to completely study the question of Hg accumulation in the Cherokee reservoir system will require information on the historical variations in Hg concentrations of the  $< 44 \mu$  sediment fraction in various locations in the lake where such sediments are and have been actively accumulating. The results of that study are pending and will be reported at a later date.

4.2.3 Mercury Distribution and Behavior in Fish and Benthos. The distribution of total mercury and percentage methylmercury in fish species and benthic invertebrate taxa collected in August 1974 at select stations is given in Tables 4.4-4.6. Mean total mercury levels well above the 0.5 ppm FDA guideline are evident in axial muscle of rockbass, hogsucker and shiners 3.1 and 21.0 km below the chlor-alkali plant, while mercury levels in rockbass 133.0 km below the plant are still in

Table 4.4. Total mercury ( $\Sigma$  Hg) and percentage methylmercury (% MeHg) in axial muscle of fish species at select stations on the North Fork of the Holston River, August 1974.

$\Sigma$  Hg =  $\mu\text{g/g}$  wet weight  $\pm 2$  S.E., % MeHg  $\pm 2$  S.E.

Species	River kilometers above (-) and below plant					
	-5.4 km		3.1 km		21.0 km	
	$\Sigma$ Hg	% MeHg	$\Sigma$ Hg	% MeHg	$\Sigma$ Hg	% MeHg
Rockbass ( <i>Ambloplites rupestris</i> )	0.70 $\pm$ 0.23 n = 13 Size 7.8 - 303.2 g	88.7 $\pm$ 8.3 n = 10 Size 7.8 - 303.2 g	1.59 $\pm$ 0.33 n = 11 Size 19.6 - 184.3 g	83.7 $\pm$ 7.0 n = 7 Size 19.6 - 184.3 g	1.14 $\pm$ 0.19 n = 16 Size 3.8 - 96.4 g	99.5 $\pm$ 4.0 n = 6 Size 3.8 - 96.4 g
Hogsucker ( <i>Hypentelium nigricans</i> )	0.46 $\pm$ 0.19 n = 11 Size 11.8 - 191.0 g	103.8 $\pm$ 3.3 n = 9 Size 11.8 - 191.0 g	1.42 $\pm$ 0.16 n = 3 Size 41.2 - 113.2 g	90.9 $\pm$ 13.8 n = 3 Size 41.2 - 113.2 g	1.23 $\pm$ 0.13 n = 6 Size 43.0 - 164.1 g	86.3 $\pm$ 5.8 n = 6 Size 45.0 - 164.1 g
Shiner ( <i>Notropis</i> spp.)	0.28 $\pm$ 0.05 n = 20 Size 7.0 - 47.1 g	84.5 $\pm$ 11.2 n = 10 Size 7.0 - 47.1 g	1.70 $\pm$ 0.51 n = 8 Size 1.6 - 3.7 g	105.1 $\pm$ 5.2 n = 3 Size 1.6 - 3.7 g	1.05 $\pm$ 0.17 n = 14 Size 1.3 - 22.2 g	83.8 $\pm$ 10.7 n = 5 Size 3.6 - 22.2 g
					0.77 $\pm$ 0.15 n = 13 Size 1.2 - 7.9 g	78.2 $\pm$ 7.3 n = 6 Size 1.6 - 4.0 g

Table 4.5. Total mercury concentration ( $\Sigma$  Hg) and percentage methylmercury (% MeHg) in benthic invertebrates collected at select stations, North Fork Holston River August 1974.

Total mercury values are ng/g wet weight (- means taxa not present in enough quantity to analyze).

River kilometers above (-) and below plant

Taxa	-5.5 km		3.1 km		21.0 km		133.0 km	
	Total Hg	% MeHg	Total Hg	% MeHg	Total Hg	% MeHg	Total Hg	% MeHg
Hydropsychidae	-	-	1680	29.17	560	41.07	-	-
<i>Corydatus</i>	88	65.91	1940	40.72	640	49.20	222	63.93
Decapoda	65	51.81	-	-	1120	48.21	270	49.11
Psephenidae	16	37.5	-	-	-	-	-	-
Composite	35	51.43	1030	83.50	840	40.48	110	-
Benthos								
Mean of taxa present <sup>a</sup>	51 $\pm$ 32	51.66 $\pm$ 11.60	1550 $\pm$ 541	51.13 $\pm$ 33.09	790 $\pm$ 250	44.74 $\pm$ 4.60	201 $\pm$ 95	56.52 $\pm$ 14.82

<sup>a</sup> Mean  $\pm 2$  S.E.

Table 4.6. Total mercury ( $\Sigma$  Hg) and percentage methylmercury (% MeHg) in axial muscle of fish species in Cherokee Reservoir, August 1974.

$\Sigma$ Hg =  $\mu\text{g/g}$  wet weight  $\pm 2$  S.E., % meHg  $\pm 2$  S.E.

Species	River kilometers below plant					
	190.0 km		238.0 km		277.0 km	
	$\Sigma$ HG	% MeHG	$\Sigma$ HG	% MeHG	$\Sigma$ HG	% MeHG
Largemouth bass ( <i>Micropterus salmoides</i> )	0.34 $\pm$ 0.16 n = 12 Size	92.5 $\pm$ 6.2 n = 10 Size	0.11 $\pm$ 0.04 n = 20 Size	80.5 $\pm$ 9.5 n = 11 Size	0.19 $\pm$ 0.04 n = 16 Size	68.5 $\pm$ 8.7 n = 10 Size
	129.6 - 2072.7 g	129.6 - 2072.7 g	19.3 - 780.0 g	19.3 - 780.0 g	57.7 - 450.6 g	57.7 - 450.6 g
Bluegill ( <i>Lepomis macrochirus</i> )	0.32 $\pm$ 0.07 n = 20 Size	82.9 $\pm$ 13.5 n = 11 Size	0.13 $\pm$ 0.03 n = 20 Size	73.6 $\pm$ 11.7 n = 10 Size	0.15 $\pm$ 0.04 n = 20 Size	70.3 $\pm$ 12.2 n = 10 Size
	35.0 - 156.3 g	35.0 - 156.3 g	11.4 - 74.5 g	11.4 - 74.5 g	6.9 - 103.3 g	6.9 - 103.3 g
Gizzard shad ( <i>Dorosoma cepedianum</i> )	0.09 $\pm$ 0.02 n = 20 Size	77.3 $\pm$ 10.9 n = 11 Size	0.06 $\pm$ 0.01 n = 20 Size	61.7 $\pm$ 14.6 n = 10 Size	0.06 $\pm$ 0.005 n = 20 Size	70.1 $\pm$ 8.3 n = 10 Size
	2.1 - 284.0	4.1 - 284.0 g	2.4 - 133.8 g	2.4 - 133.8 g	18.0 - 174.0 g	18.0 - 174.0 g
Threadfin shad ( <i>Dorosoma petenense</i> )	0.05 $\pm$ 0.005 n = 20 Size	57.9 $\pm$ 6.8 n = 10 Size	0.03 $\pm$ 0.01 n = 20 Size	54.3 $\pm$ 13.6 n = 9 Size	0.05 $\pm$ 0.01 n = 20 Size	83.8 $\pm$ 5.9 n = 7 Size
	1.1 - 4.4 g	1.3 - 4.4 g	0.5 - 15.0 g	0.9 - 2.0 g	1.2 - 48.7 g	10.3 - 48.7 g

excess of 1.0 ppm. The concentration of total mercury in rockbass and hogsucker 5.5 km above the plant approach or exceed 0.5 ppm which was unexpected for this control area. It is possible that localized movement of these species to and from the contaminated area below the plant could explain these slightly elevated levels. Fish species collected in Cherokee Reservoir on the whole contain muscle mercury below 0.5 ppm (Table 4.5).

Our observation that the majority of total mercury in fish muscle in the Holston-Cherokee system is methylmercury is in agreement with other investigators<sup>12-19</sup> (Tables 4.4 and 4.5).

Estimates of total mercury and percentage methylmercury in benthic invertebrate taxa collected in August 1974 on the North Fork are given in Table 4.6. Benthic invertebrates 3.1 km below the plant contain total mercury at about the same level (mean  $1.550 \pm 0.271$   $\mu\text{g/g}$ ) as fish species (Table 4.4). Total mercury in benthic invertebrates 5.5 km above and 21.0 and 133.0 km below the plant appears to be lower than fish species at these stations (Tables 4.4 and 4.6). Mean percentage methylmercury in benthic invertebrates at all stations was on the order of 50% (Table 4.6) but considerable variability exists between taxa at any given station. The finding that on the order of 50% of total mercury in benthic invertebrates is methylmercury suggests that fish species in this system may derive a significant proportion of their methylmercury burden through feeding on benthic invertebrates.

Rockbass are predators feeding primarily on benthic invertebrates and smaller fish. Hogsuckers are bottom feeders and undoubtedly ingest benthic invertebrates as well as sediment. Shiners are predominately

insectivorous feeding on benthic invertebrates. The potential food web consisting of rockbass-shiner-benthic invertebrate in the North Fork enables a qualitative examination of food chain concentration of total mercury. At the 3.1 km below the plant all links in this chain have approximately the same mercury levels (Tables 4.4 and 4.5) indicating mercury is not being magnified at the station most contaminated with mercury. Mercury contamination due to sediments in the G. I. tract of invertebrates may, however, mask this phenomenon. At the stations 5.5 km above and 133.0 km below the plant it appears that mercury concentration may increase with trophic level for these three taxa (Tables 4.4 and 4.5). It is possible that under high mercury contamination, available mercury in water and sediments causes trophic accumulation of mercury to be masked by direct accumulation from water.

Although incomplete, analyses of total mercury levels in fish species collected in August 1975 (Table 4.7) indicate levels downstream from the plant remain elevated. In 1975 we sampled farther upstream (9.0 km) above the plant and it appears mercury levels are lower than at 5.5 km in 1974 (Tables 4.4 and 4.7).

The concentration of total mercury in fish species and benthic invertebrates collected in August 1974 appears to follow the concentration of total mercury in the water column and bed sediments at the four stations sampled (Fig. 4.3). When the remaining samples of our 1975 collection are analyzed we will, through multivariate analysis determine which factors in the abiotic environment account for the variability in total mercury levels in fish species in this system.

Table 4.7. Total mercury concentration ( $\Sigma$  Hg) in axial muscle of fish species collected at select stations in the North Fork Holston River and Cherokee Reservoir in August 1975.

$\Sigma$  Hg =  $\mu\text{g/g} \pm 2$  S.E.

Species	North Fork Holston kilometers above (-) and below plant					Cherokee 277.0 km $\Sigma$ Hg
	-9.0 km $\Sigma$ Hg	3.1 km $\Sigma$ Hg	21.0 km $\Sigma$ Hg	43.0 km $\Sigma$ Hg	133.0 km $\Sigma$ Hg	
Rock bass ( <i>Ambloplites rupestris</i> )	0.32 $\pm$ 0.09 n = 10 Size 9.3 - 133.9 g	---	---	1.29 $\pm$ 0.19 n = 10 Size 6.1 - 165.4 g	1.12 $\pm$ 0.57 n = 10 Size 42.0 - 112.7 g	---
Hogsucker ( <i>Hypentelium nigricans</i> )	0.28 $\pm$ 0.13 n = 10	2.14 $\pm$ 0.59 n = 10	1.66 $\pm$ 0.21 n = 10	1.11 $\pm$ 0.17 n = 10	0.82 $\pm$ 0.36 n = 10	---
Shiner ( <i>Notropis</i> spp.)	15.3 - 274.2 g 0.12 $\pm$ 0.03 n = 5 Size 7.8 - 12.0 g	36.3 - 311.4 2.12 $\pm$ 0.72 n = 5 Size 1.7 - 2.7 g	37.4 - 250.3 g 1.34 $\pm$ 0.51 n = 5 Size 9.2 - 11.2 g	18.2 - 471.1 g 1.43 $\pm$ 0.53 n = 4 Size 8.3 - 13.2 g	48.6 - 385.4 g 0.52 $\pm$ 0.51 n = 5 Size 8.4 - 12.3 g	---
Largemouth bass ( <i>Micropterus salmoides</i> )	---	---	---	---	---	0.11 $\pm$ 0.09 n = 10 Size 23.9 - 1020.5 g
Bluegill ( <i>Lepomis macrochirus</i> )	---	---	---	---	---	0.10 $\pm$ 0.02 n = 10 Size 11.6 - 139.0 g
Gizzard shad ( <i>Dorosoma cepedianum</i> )	---	---	---	---	---	0.05 $\pm$ 0.007 n = 10 Size 133.7 - 250.79

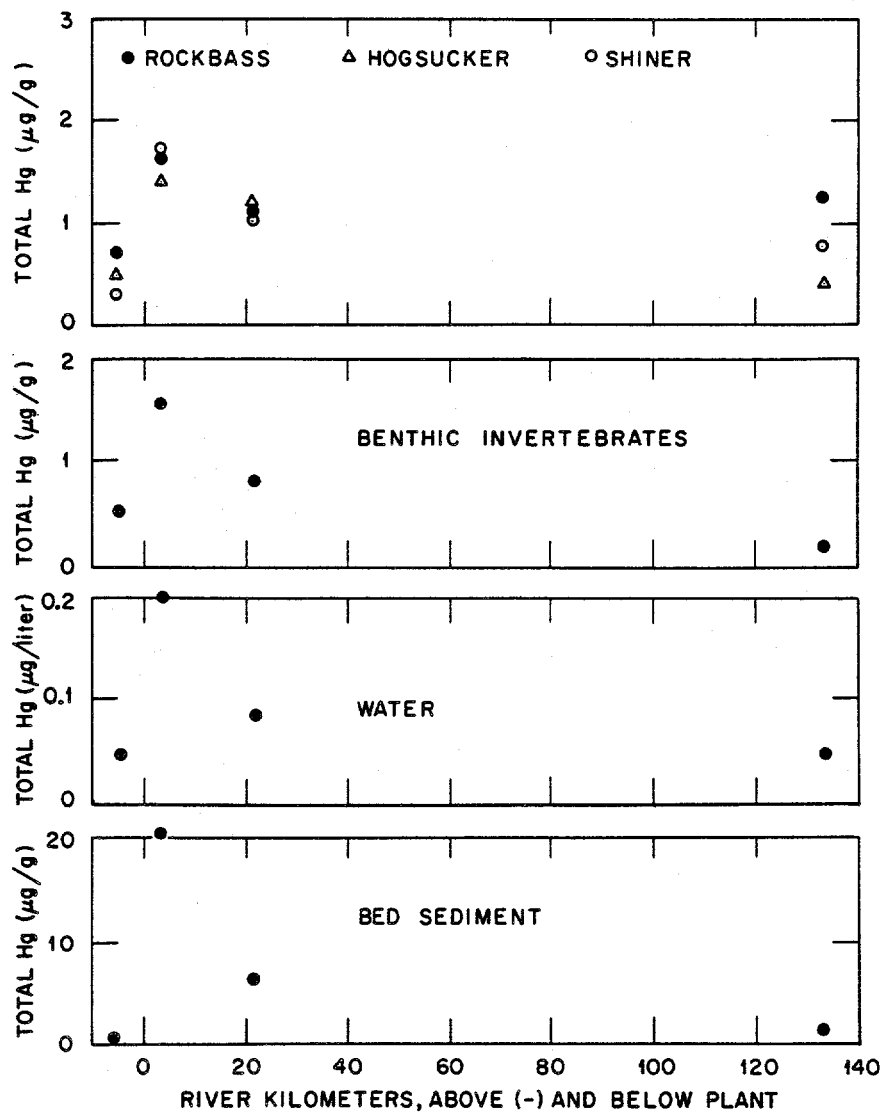


Figure 4.3 Distribution of total mercury in fish axial muscle (wet weight), benthic invertebrates (wet weight - whole animal), water (unfiltered) and bed sediment ( $< 44 \mu$  dry weight) above and below the chlor-alkali plant on the Holston River in 1974. Water and sediment data are from Reference 2.

In addition on-going research on the accumulation of mercury by fish species from sediments and the effect of organic ligands on mercury accumulation will provide a better understanding of the mechanisms of mercury uptake by aquatic biota. A report of work still in progress will be submitted at a later date.

4.2.4 Mass Balance for Mercury Near Saltville, Virginia. Accurate quantification of the present rates of aqueous mercury input to the NFHR from the waste pond system near Saltville is essential to the consideration of continued contamination of the endemic biota and evaluation of any future abatement measures. Leaching rates of mercury from the abandoned plant waste disposal ponds were estimated during two hydrologically contrasting periods (May 1975, river discharge at river km 3.1,  $12 \text{ m}^3/\text{sec}$  and pond surfaces partially inundated with water; and July 1975, river discharge  $1.8 \text{ m}^3/\text{sec}$ , pond surfaces dry, seepage outfalls exposed). Using the mass balance approach, leaching rates of mercury from the waste disposal ponds were calculated as the difference between upstream and downstream instantaneous mercury fluxes (in mass/time units) assuming steady state conditions (Table 4.8). Based on mass balance calculations from both sampling periods the flux of mercury in the NFHR increases by a factor of approximately 30 between upstream (at river km -2.7) and downstream (at river km 6.4) sites. It is also evident that the net flux of mercury from the waste pond area does not exhibit a linear relationship with river discharge. For example, although dis-

Table 4.8. Summary of mass balance determinations of mercury leaching rate from the chlor-alkali plant waste disposal pond area, North Fork of the Holston River.

Date	Upstream <sup>a</sup>			Downstream <sup>b</sup>				Net flux (g/day)
	Total Hg ( $\mu\text{g/l}$ )	Stream discharge <sup>c</sup> ( $\text{m}^3/\text{sec}$ )	Total Hg flux (g/day)	Total Hg ( $\mu\text{g/l}$ )	% dissolved	Stream discharge <sup>c</sup> ( $\text{m}^3/\text{sec}$ )	Total Hg flux (g/day)	
5-21-75	0.003	11.5	2.98	0.094	52	12.2	99.1	96.1
7-29-75	0.006	1.70	0.88	0.167	45	1.92	27.7	26.8
7-30-75	0.007	1.61	0.98	0.185	27	1.81	28.9	27.9
7-31-75	0.008	1.57	1.09	0.193	38	1.77	29.5	28.4
7-31-75								14.2 <sup>d</sup>

<sup>a</sup>2.7 km above old chlor-alkali plant.

<sup>b</sup>6.4 km below old chlor-alkali plant.

<sup>c</sup>Obtained by factoring discharge at USGS Sta. 03488000 located near Saltville by drainage area increase.

<sup>d</sup>Based on summation of measured fluxes of seepages from waste pond #5 and the major outfall from pond #6.



charge was lower by a factor of 6.8 between the May and July measurement periods the net flux of mercury was lower by only a factor of 3.6. This may indicate that other factors such as antecedent hydrologic conditions of the waste ponds influence the Hg flux from this area.

Direct measurement of the mercury flux (14.2 g/day) from exposed seeps of the waste ponds on July 31, 1975 offers reasonable verification of the net fluxes calculated by upstream-downstream mass balance for the same period (28.4 g/day). Although this measured flux is only about half the calculated flux the agreement is not unreasonable given that only the most obvious and accessible seepages were measured. In any case these measurements and calculations point to the continued significance of the waste pond area as a source of Hg.

4.2.5 Laboratory Studies On Waste Pond Material. Very little is known about the horizontal and vertical distribution of mercury in the waste ponds or about the solubility of mercury in the waste material. It has previously been reported<sup>3</sup> that total mercury concentration in waste solids from the ponds is as high as 150 µg/g. More recent measurements at depths from 0-1.8 m in the waste ponds have revealed concentrations up to 350 µg/g. In order to determine what fraction of the total mercury in the waste is readily leachable by rainwater or actually dissolved in the interstitial water, waste material from the top and bottom of short cores collected in each pond was leached for 96 hours with rainwater. Table 4.9 summarizes the relevant results of this experiment as well as the experimental conditions. The most important implication of this simple experiment is that only a very small percentage (< 2% for Pond #5 and < 0.1% for Pond #6) of the waste-

Table 4.9. Summary of laboratory mercury leaching experiment using material from the chlor-alkali plant waste disposal ponds

Values are means of duplicate experiments.

Sample location and depth	Total Hg in waste ( $\mu\text{g/g}$ )	Leachate pH	Leachate specific conductance ( $\mu\text{mhos/cm}$ )	Leachate $\text{Cl}^-$ (mg/l)	Leachate dissolved Hg ( $\mu\text{g/l}$ )	% waste soluble <sup>a</sup>	% total Hg soluble <sup>b</sup>
Pond #5 0-2 cm	230	8.6	240	45	$6.4 \pm 1.2$	1.2	0.14
Pond #5 36-38 cm	160	10.2	841	122	$54.5 \pm 6.5$	4.4	1.78
Pond #6 0-8 cm	124	9.8	268	55	$1.2 \pm 0.2$	1.6	0.05
Pond #6 8-27 cm	37	9.2	985	170	$5.0 \pm 0.7$	5.8	0.07

<sup>a</sup>Two grams of waste material were shaken for 96 hours at ca. 25°C with 100 mls. of rainwater having pH = 3.8, conductance = 41  $\mu\text{mhos/cm}$ , chloride = 0.03 mg/l and total Hg = 0.13  $\mu\text{g/l}$ .

<sup>b</sup>Uncorrected for material dissolved in natural moisture of samples.

associated mercury was solubilized under the experimental conditions. This soluble fraction likely consists of aqueous mercury deposited when the pore water was removed during drying of the waste as well as readily soluble mercury associated with the solid material. It is also significant that concentrations of mercury observed in the leachate ( $30 \pm 28$   $\mu\text{g/l}$ ) were similar to observed concentrations in seepages from Pond #5 ( $40 \pm 24$   $\mu\text{g/l}$ ).

Although the total quantity of mercury remaining in the waste pond system cannot be accurately determined from our data, we can make an estimate based on core data from Pond #5. Mercury concentrations in these cores were found to be highest in the upper portion (350 to 4.4  $\mu\text{g/g}$  from 0-200 cm depth) but averaged 92  $\mu\text{g/g}$  ( $\sigma = 91$ ,  $N = 17$ ). An estimate of the total mercury burden of the upper two meters of Pond #5 can thus be calculated. Using the pond surface area of  $2.9 \times 10^5 \text{ m}^2$  and assuming a waste density of  $2.0 \text{ g/cm}^3$  leads to a waste mass of  $\sim 10^9$  kg. If the mercury content of this mass indeed averages 92  $\mu\text{g/g}$

then the total mercury burden of the upper two meters of Pond #5 is  $\sim 9 \times 10^4$  kg. Assuming that less than 1% of this mercury is dissolved or readily soluble and using the leaching rate of mercury measured on July 31, 1975 for Pond #5 (14 g/day) we conclude that it would take on the order of  $10^2$  years to totally deplete Pond #5 of its soluble mercury burden. Since only the upper two meters of this pond were considered as a source for mercury in this calculation the estimate of flushing time is obviously minimal. Even so, the calculation points to the potential persistence of the mercury problem on the NFHR in the absence of abatement measures.

4.2.6 Atmospheric Emission of Mercury From Waste Ponds. Elemental mercury ( $\text{Hg}^0$ ) is known to be a substantial fraction of the atmospheric mercury burden, especially near geothermal areas and mercury ore deposits.<sup>20,21</sup> Because of the high volatility of  $\text{Hg}^0$  as well as various organomercurials it is widely dispersed in the earth's atmosphere. Recently several papers have appeared concerning atmospheric Hg distributions in natural source areas,<sup>20,21</sup> ambient air in major cities distant from such areas,<sup>22</sup> and various sites known to be impacted by coal-fired power generation plants.<sup>23-25</sup> However, no information on such distributions or actual emissions from chlor-alkali plants or associated waste ponds exists, although studies concerning levels of  $\text{Hg}^0$  within certain workroom areas of the plants have been reported.<sup>26,27</sup>

We established an aerosol sampling station between the two waste ponds (Fig. 4.1) which would receive the greatest possible exposure to any emitted vapors. We collected duplicate samples of mercury vapor in filtered air (glass columns containing activated charcoal),<sup>28</sup> bulk

deposition (glass bottles), and total aerosol ( $0.4 \mu$  nuclepore filter collectors) from 1200 hrs. on 7/29/75 to 0700 hrs. on 8/1/75. The results of the experiment are given in Table 4.10. For the period sampled, wind direction recordings indicated the prevailing wind pattern to be directly across waste pond #5 for 67% of the time (i.e., a NE wind), across pond #6 for 17% of the time (SW wind), and from other directions or calm for 16% of the time. The particulate Hg load was quite low considering the area in question and may reflect the stability of the waste pond surface to dust resuspension. The concentrations reported here ( $0.30 \pm 0.05 \text{ ng/m}^3$ ) compare with values in the range of  $1\text{--}9 \text{ ng/m}^3$  reported for ambient air in industrialized cities<sup>29</sup> and with values in the range of  $0.07\text{--}0.15 \text{ ng/m}^3$  in Walker Branch Watershed.<sup>30</sup> The actual concentration of Hg on the aerosols in the wastepond area expressed as ng of Hg per mg of particulate (ppm) is  $5.7 \pm 0.7$  ppm compared to  $4.0\text{--}8.8$  ppm for Walker Branch Watershed aerosols. Thus there appears to be no significant elevation in particulate Hg in the air near the waste ponds during the period sampled.

Of most interest are the relatively high concentrations of gaseous Hg measured. These values ( $991 \text{ ng/m}^3$ ) compare with concentrations in the range of  $0\text{--}49 \text{ ng/m}^3$  for air in the Tampa, Florida area<sup>22</sup> with  $12 \pm$

Table 4.10. Estimates of atmospheric emission of mercury from the chlor-alkali plant waste disposal ponds.

Sample	Flow rate (l/min)	Volume sampled ( $\text{m}^3$ )	Total particulates ( $\mu\text{g/m}^3$ )	Hg load ( $\text{ng/m}^3$ )
Hg vapor #1	1.85	2.52	—	990
Hg vapor #2	1.77	2.41	—	992
Total aerosols #1	10.5	42.8	58.4	0.25
Total aerosols #2	9.3	38.1	63.0	0.36

7 ng/m<sup>3</sup> for air in Walker Branch Watershed, and with the EPA ambient air standard for total Hg of 1000 ng/m<sup>3</sup>. Our finding that essentially 100% of the Hg in ambient air is present as a vapor agrees well with reported EPA tests (96% as vapor).<sup>31</sup>

It is possible to extrapolate the gaseous Hg results to determine an approximate emission rate for the waste pond area. However, an experiment has been designed to actually measure emissions from a known surface area of the waste ponds and will be reported at a later date. The important finding to date is that a previously unsuspected pathway for release of Hg from the waste pond area has been discovered, and that from July 29 to August 1, 1975 the air passing from waste Pond #5 to our adjacent sampling station approached the EPA ambient air limit for total mercury.

#### 4.3 Walker Branch Watershed Studies

4.3.1 Introduction and Methods. There is mounting evidence<sup>32-36</sup> that many activities of man, particularly combustion of fossil fuels and industrial processing of metals and their ores, are responsible for elevated concentrations of many trace metals in the atmosphere and therefore potentially increased rates of transport to, and accumulation in, the landscape. Work of this project relates directly to quantification of atmospheric input, landscape cycling and hydrologic output of selected trace metals for the 97.5 hectare Walker Branch Watershed (WBW) which is impacted locally by emissions from three coal-fired steam plants. Specifically our research has the following objectives: 1) to derive relationships between levels of selected trace metals in air,

rain aerosols, soil and rock and by these data and the known atmospheric emissions, differentiate between natural and anthropogenic origins; and 2) to understand the mechanisms that control landscape input, cycling and output for several trace elements.

The facilities at WBW and previous research related to this subject have been described elsewhere.<sup>37-40</sup> Methods pertaining to our research on trace metal geochemistry on WBW have already been outlined in earlier progress reports<sup>1</sup> and given in detail by Andren et al.<sup>30</sup> However, during the preceding year several procedures and analytical techniques have been modified in an effort to improve the quality of data generated. Acquisition of a Perkin-Elmer Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) provided the analytical sensitivity to permit direct determination of trace metal concentrations in rain and stream water, thus eliminating some of the potential contamination difficulties inherent in the previously used solvent-extraction atomic absorption technique. The GFAAS also permitted collection of much smaller water samples than were required for the extraction technique. Routine rain and stream sampling were discontinued in favor of sampling of discrete meteorologic-hydrologic events with the purpose of better discovering useful relationships between trace metal concentrations and hydrologic/meteorologic parameters.

All data for trace element concentrations in stream water from WBW have been paired with instantaneous stream flows for each sampling time and the resulting interactions studied. This pairing also permitted calculation of discharge-weighted mean concentrations for each trace element (dissolved and particulate) and determination of the

representativeness of stream sampling. The six-month mass balance<sup>1,30</sup> for selected trace metals on WBW has been improved by using more reliable concentrations of selected metals (e.g., Cd in rain input) obtained during the preceding year and by recalculating the watershed output of these metals for the six-month period using discharge-weighted mean concentrations.

4.3.2 Atmospheric Input and Mechanisms. The annual atmospheric discharge of 37 elements from local coal-fired steam plants, including the seven trace elements analyzed in stream flow, has previously been estimated<sup>30</sup> for the Oak Ridge area. Aerosols, composed partially or entirely of these elements, may be removed from the atmosphere by 1) wet deposition (rain, snow, sleet, fog, etc.), 2) sedimentation (gravitational settling) and 3) impaction on obstacles (e.g., vegetation). Work during this reporting period continued to focus on quantifying wet deposition and impaction.

4.3.2.1 Wet Deposition. Weighted mean concentrations of selected trace metals in rain on WBW measured by GFAAS during the preceding year are given in Table 4.11 where they are compared with concentrations used

Table 4.11. Precipitation weighted means of trace element concentrations in rain ( $\mu\text{g/l}$ ) on Walker Branch Watershed (WBW)

Element	Rain gauge #1 (west subbasin)	Rain gauge #3 (east subbasin)	WBW ('75) <sup>a</sup>	WBW (ref. 30) <sup>b</sup>	WBW (ref. 30) WBW ('75)
Cd	0.22	0.77	0.94	7.0	7.4
Cu	4.0	4.9	4.3	15.7	3.7
Cr	1.2	0.68	0.96	1.9	2.0
Pb	4.8	10.1	7.0	12.9	1.8
Mn	5.2	2.0	4.6	12.8	2.8
Zn	26.6	34.2	30.4	27.5	0.9
Hg	0.62	0.41	0.52	0.17	0.3

<sup>a</sup><sub>n</sub> = 8 (Cd, Cu, Cr, Zn), <sub>n</sub> = 4 (Pb, Zn, Mn); period from February to August 1975.

<sup>b</sup><sub>n</sub> = 12; period from January to June 1974.

by Andren et al.<sup>30</sup> to calculate a six-month mass balance for WBW. Within the obvious limits set by the smaller number of observations during the current year, the agreement between these data sets is not unreasonable except for cadmium and perhaps copper. Although we cannot positively identify the reason for the discrepancies between these data sets, we speculate that differences in various procedures (e.g., length of time that rain samples remained in field, the condition with respect to corrosion of the metal surfaces of the Wong samplers, and analytical techniques employed) may have been responsible. Galloway and Likens<sup>41</sup> have recently presented findings concerning the many problems related to the collection and storage of precipitation samples. Specific problems identified with the type of Wong collector we used were the large metal area available for precipitation "splash off" into the collector vessel and the air gap between the sliding lid and collection vessel which may allow dry deposition to contaminate precipitation samples. Fortunately the bulk of the new data presented here was collected with both these problems relatively minimized (exposed metal surfaces, except sensor head, were coated with epoxy paint and the sliding lid was modified to minimize air gap). New precipitation collectors (USAEC-type) which seal positively and which minimize use of contaminate metals in their construction are presently under construction for use on WBW.

Under the assumption that the cadmium concentrations in wet deposition as given in earlier reports<sup>1,30</sup> were in error by a factor of  $\sim 7$  due to contamination problems, we have recalculated the six-month wet deposition input of cadmium to WBW (by applying this factor to the previously reported value of 62.4 g/ha) as 8.9 g/hectare. This correc-



tion represents a seven-fold decrease in the wet deposition of cadmium and has significant consequences in the corrected six-month mass balance for this element presented in a later section.

4.3.2.2 Aerosol Chemistry. Aerosol research during the past year has been concentrated in the areas of technique development and validation. The bulk of the aerosol chemistry data reported previously<sup>1</sup> and subsequently utilized in calculations of cycling budgets for WBW<sup>30</sup> and in determinations of sources of aerosols<sup>42</sup> represented total samples collected using Hi-vol samplers. Since such samplers are suspected of contamination problems<sup>43</sup> we have recently tested low flow vacuum pumps (14-28 l/min) in conjunction with all glass or all stainless steel membrane filter holders for collection of total aerosols (equivalent aerodynamic diameter of  $> 0.25 \mu$ ) at three sites in the watershed. This has allowed for comparison of temporal, spatial, and inter-technique variability. In all cases samples were collected within 1 m of the ground and were protected from wetfall as well as direct gravitational settling of large ( $> 10 \mu$ ) particles.

Table 4.12 summarizes total aerosol concentrations of selected elements collected by various techniques as well as computed ranges based on steam plant emission data manipulated using the Atmospheric Transport Model, (see Section 3.2.1 of this report for details). In view of some uncertainty in the July 1974 data (e.g., problems associated with Hi-vol samplers, a limited number of samplers and collection sites, and short duration of sampling period) it is reassuring to observe the reasonably close agreement among samples A-D. Of special importance is the excellent agreement between the samples collected simultaneously at

Table 4.12. Comparison of measured<sup>a</sup> and calculated<sup>b</sup> air concentrations of selected elements in Walker Branch Watershed

Element	Concentrations (ng/m <sup>3</sup> )						Over lap
	Computed range	A	B	C	D	E	
Al	655-2800	823	655	714	709	725 (10)	Y
As	0.28-3.03	1.35	1.49	1.52	1.18	1.39 (14)	Y
Br	0.23-3.25	23	12.2	8.3	8.6	13.0 (52)	N
Ca	273-1668	472	174	92.8	109	212 (83)	Y <sup>c</sup>
Cd	0.03-0.54	4.1	<8	4.3	4.2	4.2 (2)	N
Cr	0.88-3.9	1.7	1.8	2.0	2.2	1.4 (23)	Y
Cu	0.50-3.25	8.2	<5	<9	<9	<8	?
Fe	683-4160	313	232	274	245	266 (14)	N
Hg	0.008-0.043	0.13	0.15	0.07	0.07	0.11 (36)	N
K	97-346	223	189	207	204	206 (7)	Y
Mn	2.14-10.6	14	7.2	14.0	11.8	11.8 (27)	Y <sup>c</sup>
Na	32-151	201	97.7	124	121	136 (33)	Y
Pb	0.31-7.6	90	-	-	-	90	N
Se	0.13-0.48	1.05	1.6	0.98	0.94	1.1 (27)	N
Ti	32-151	66	28	36	28	39.5 (46)	Y
V	1.8-7.15	3.6	3.7	2.4	2.3	3.0 (27)	Y
Zn	2.9-59	23.4	17.2	14.5	15.4	17.6 (23)	Y

<sup>a</sup>Measured values:A - total sample, Hi Vol collector, west weir, July 1974 (Andren et al., 1975<sup>30</sup>).

B - total sample, nuclepore filter collector, rain gauge #5, 2/14-2/21 1975.

C - total sample, nuclepore filter collector, between rain gauges #2 &amp; 3 under canopy, 3/20-4/3 1975.

D - total sample, nuclepore filter collector, rain gauge #5, 3/20-4/3 1975.

E - mean and coefficient of variation (in parentheses) for values A-D.

<sup>b</sup>Calculated values - see Figure 3.7 and associated text (R. J. Raridon, pers comm.)<sup>c</sup>Agreement is within  $\pm 1 \sigma$  of  $\bar{x}$ .

two sites, one beneath and one outside of the forest canopy (samples C and D). This indicates that, on a fairly long time scale (14 days), the air mass within the watershed was well mixed and that, during this time period, local soil and dust sources were minimized. This is of interest in the design of future experiments but will require further verification.

The last column of Table 4.12 compares the mean measured values with the concentration ranges attributed to emissions from the nearby steam plants. The elements which show an enrichment in WBW air over that expected to be contributed from the steam plants are Br, Cd, Hg, Pb, and Se. Significantly, these are all elements which are associated with combustion processes and hence are generally found to be concen-

trated on the smallest sized particles which have the longest atmospheric residence times.<sup>43-46</sup> Thus, it is plausible that these elements reflect the importance of long-range transport over local sources to the air mass in WBW. In addition this group of elements was previously calculated as being enriched in Walker Branch Watershed aerosols compared to soil sources.

In a more recent paper<sup>42</sup> we have applied a chemical mass balance approach<sup>47,48</sup> to calculate a "model aerosol" which was seen to be very close in chemical composition to that measured during July 1974. With this model, which approximates contributions to the aerosols in WBW from soil, auto, and steam plant sources using Al as a tracer, we could account for only 1% of the Cd and Hg, and 50% of the Se as originating from local soil and coal combustion sources while we could account for 77% of the Br and 100% of the Pb as being from local automobile emissions. Thus it appears that, of the elements for which the ATM shows poor correlation between observed and measured concentrations, Br and Pb can be attributed to automotive sources while Cd, Hg, and Se can be attributed to long-range transport of fine particles in the atmosphere.

4.3.3 Watershed Output and Mechanisms. Sampling of WBW springs and streams for trace metal content has two basic purposes: 1) to understand the mechanisms controlling concentrations, and thus the hydrologic transport, of these metals in stream water and 2) to accurately quantify the annual export of these metals from the watershed. Analysis of existing data and results acquired during the current year have indicated the relative importance of instantaneous stream discharge as a concentration-controlling variable for dissolved trace metals.

Such relationships have been reported for other watershed areas.<sup>49-51</sup> For example, simple product-moment correlations between instantaneous stream discharge and concentrations of chromium, nickel and lead at the west spring site; between discharge and copper, nickel and lead at the east spring site; and between discharge and cadmium and lead at the west fork outlet, were weak ( $r = -0.30$  to  $-0.56$ ) but significant ( $p \leq 0.10$ ) and consistently negative indicating a dilution effect by increasing stream discharge. A basis which integrates many factors and may better represent the overall moisture status of the watershed than instantaneous stream discharge involves the relationships between average trace metal concentrations and season of year (Fig. 4.4). These correlations

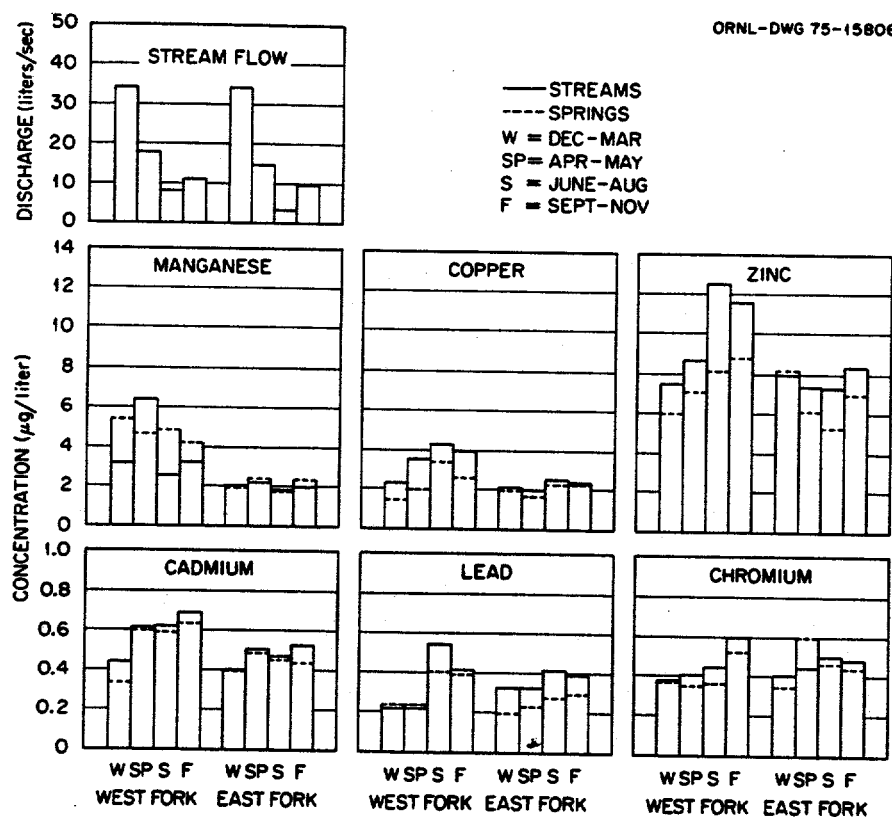


Figure 4.4 Seasonal variations in mean concentrations of selected trace metals in Walker Branch springs and streams.

demonstrated a significant trend in one fork (west) but not in the other (east). Figure 4.4 indicates that concentrations of all trace metals, except manganese, were higher during periods of lowest total stream flow at both sampling sites in the west fork but comparatively constant in the east fork.

The behavior of most dissolved trace metal concentrations at the west fork sites is generally consistent with the Nernst law<sup>52</sup> relating the rate of dissolution of rocks to the saturation deficit. On a landscape basis the Nernst law applies to the entire litter-soil-rock system wherein concentrations of trace metals in waters of the saturated zone are controlled, within limits set by the composition of the solid phase, by the residence time of these waters within the system. Since winter stream flow represents water which resided within the litter-soil-rock system for the shortest period of time it has acquired the lowest burden of trace metals.

The behavior of dissolved trace metals at the east fork sites reflects a reasonably well-buffered system with little seasonal variability in spite of large variability in hydrology. It has been suggested,<sup>53</sup> based on comparative studies of hardness and temperature variability, that the aquifer feeding the east spring is of the conduit-flow type and thus residence time of water in this system may be shorter than in the west system. If the latter is true, one would expect concentrations of some solutes in the east spring to be somewhat lower than in the west spring but not necessarily less variable, as indicated in Figure 4.4. Thus the concentration-buffering mechanisms operating in the east aquifer must be capable of overriding any effects due to water

extrapolation. Thus while this approach reveals that stream flows were sampled reasonably representatively during the period from January to June 1974 (period of mass balance calculations), this period was hydrologically atypical of the entire year. There are other obvious reasons for not extrapolating the six-month mass balance calculations to an annual basis, such as those related to the importance of stream transport of fallen leaves and their decomposition products in the latter half of the year, but hydrologic reasons alone are sufficient.

The adjusted trace element mass balances for the period January to June 1974 are summarized in Table 4.13, along with the relative retention coefficients (percent of input retained by watershed) for each element. The major differences between these mass balances and those reported earlier for the same period<sup>1,30</sup> are the decreased cadmium atmospheric input and the slightly higher stream outputs of all trace elements. These changes result in a much lower retention coefficient for cadmium (63% versus 94%) which is in better agreement with the higher mobility of this element compared to lead in litter and soils.<sup>55</sup> For the other trace metals the retention coefficients were generally only slightly lower than those calculated earlier.

The possible consequences of net gains of certain trace elements by WBW can be estimated through calculations of enrichment factors and doubling times for various components of the watershed. Using biomass data for three sizable ecosystems compartments, total living vegetation, litter, and soil along with data on the initial standing pool of Cd, Pb, and Zn in each compartment,<sup>56</sup> we have constructed Table 4.14. Soil pools have been estimated using an active soil depth of 75 cm (approx-

Table 4.14. Effect of net gain of Cd, Pb and Zn by WBW on various components of the ecosystem<sup>a</sup>

	Total living vegetation	Litter (O <sub>1</sub> + O <sub>2</sub> )	Total vegetation	Soil profile (to 75 cm)
Biomass (10 <sup>3</sup> kg/ha)	155.7	23.2	178.9	9 × 10 <sup>6</sup>
Initial standing pool (gm/ha)				
Cd	25	13	38	1.1 × 10 <sup>3</sup>
Pb	341	853	1194	7.8 × 10 <sup>4</sup>
Zn	1102	1972	3074	1.2 × 10 <sup>5</sup>
Enrichment ratio				
Cd	1.3 (3.4) <sup>b</sup>	1.5 (5.6) <sup>b</sup>	1.2 (2.6) <sup>b</sup>	1.0 (1.0) <sup>b</sup>
Pb	1.4	1.2	1.1	1.0
Zn	1.2	1.1	1.1	1.0
Doubling time (yrs.)				
Cd	1.9 (0.2)	1.0 (0.1)	2.9 (0.3)	83 (9)
Pb	1.2	3.0	4.2	277
Zn	2.8	5.0	7.7	302

<sup>a</sup>Based on a 6 month net retention in the watershed of Cd = 6.6 gm/ha, Pb = 140 gm/ha, Zn = 200 gm/ha.

<sup>b</sup>Values in parentheses from ref. 30.

mate root zone depth),<sup>57</sup> an average soil bulk density of 1.2 g/cc<sup>39</sup> and WBW soil elemental concentrations<sup>58</sup> (Cd = 0.12 µg/g; Pb = 8.6 µg/g; Zn = 12.8 µg/g). The enrichment ratio is defined as the relative increase in the trace metal pool in any one compartment assuming the entire watershed six-month net gain of that trace metal is absorbed by one compartment (calculated as: concentration after six months enrichment/concentration before enrichment). Doubling time is defined as the number of years required for any compartment to double its initial trace element concentration, making the same above assumptions (calculated as: initial standing pool/annual net gain). Although it is unlikely that any element is entirely accumulated by an individual compartment, it is nevertheless interesting to compare the results of these calculations for Cd, Pb, and Zn.

If we assume that an enrichment ratio of > 1.5 is detectable, then only Cd would approach showing an accumulation, that being in the litter

pool. However, recent data<sup>1,55</sup> suggest that for certain soils Cd is more soluble in the organic litter layer than Pb and thus moves more rapidly into the soil. If this assumption is made for WBW soils it is obvious that over the six-month time scale no trace element enrichments would be detectable. The doubling times, also calculated in Table 4.14, are relatively short for Cd in the living vegetation and litter compartment, and are also quite small for Pb and Zn in the living vegetation. However, since uptake for these elements is likely divided among all these compartments, with the bulk eventually entering the soil compartment, it is apparent that a net gain of trace elements by the watershed probably would not manifest itself in the soil profile for a number of years, although enrichments in the upper soil horizons may show up more rapidly.

#### 4.4 Biological Effects and Distribution of Heavy Metals on Crooked Creek Watershed

4.4.1 Introduction. Crooked Creek Watershed is an important focal point for environmental studies of heavy-metal effects on forested ecosystems. The watershed is a 466 ha area within the Clark National Forest of southeastern Missouri located 24 miles east of Salem, Missouri, in Iron County. This portion of Missouri, known as the "New Lead Belt," is the world's largest lead-producing region.

The watershed itself lies on the Springfield-Salem Plateau, an area characterized by hills alternating with steep valleys. Canopy vegetation is largely oak species (black oak, white oak, and northern red oak) with a smaller portion of shortleaf pine. A primary Pb smelter, operated by



American Metals Climax (AMAX) and situated at the apex of the triangularly shaped watershed, has been in operation since 1968. Both smelter stack emissions and associated fugitive particulates are the main source of heavy metal contamination on CCW.

Crooked Creek Watershed is a unique site for trace contaminant fate and effects because 1) a single point source has contaminated the area leaving a gradient of heavy metal concentrations with distance from the smelter, 2) the natural ecosystem remains largely intact with little damage due to burning or other drastic perturbations, and 3) the watershed has been well defined geographically and monitored for heavy metals for the past four years.

The objectives of this study are 1) to elucidate the fate of smelter emissions deposited on a forest landscape, and 2) to evaluate the effects of heavy metals on various ecosystem components of the watershed. A sampling strategy (Fig. 4.6, see also Fig. 3.10) based on distance from the smelter stack and windrose patterns was developed to obtain samples for statistical comparisons. During the past year, we have focused our attention on the fate and effects of smelter emissions on the following watershed components: 1) invertebrates, 2) litter-inhabiting microbes, 3) litter, 4) tree roots, and 5) above-ground vegetation.

4.4.2 Fate of Heavy Metals. The primary inputs of heavy metals on the forest floor are: 1) direct impaction of airborne particulates on exposed soil or litter, and 2) annual litterfall of leaves which contribute assimilated metals and particulates impacted on leaf surfaces.

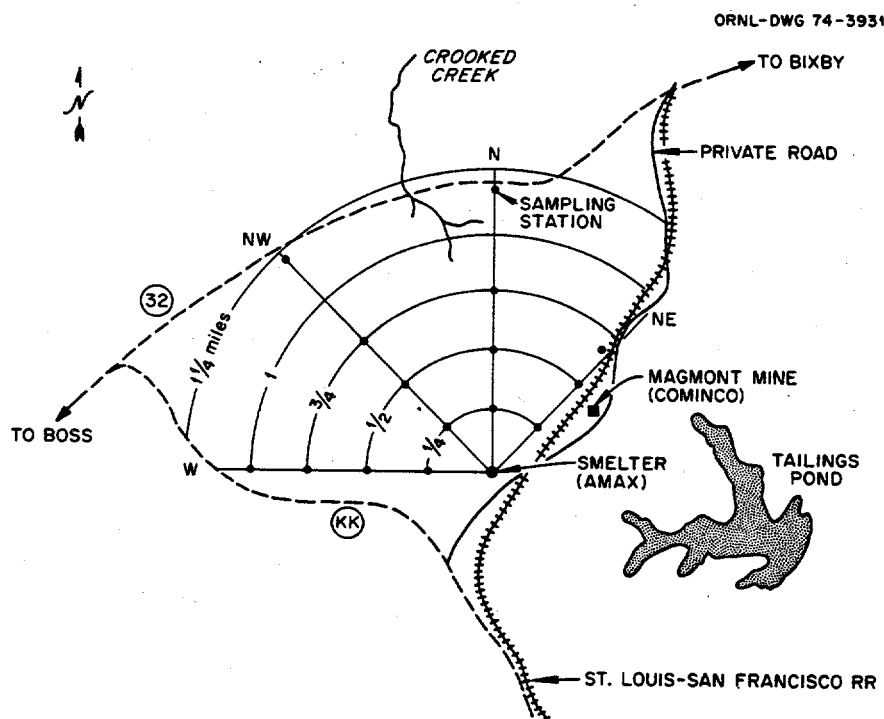


Figure 4.6 Sampling grid on Crooked Creek Watershed in southeastern Missouri (Clark National Forest; Iron County, Mo.).

The greatest accumulation of heavy metals in biological components occurred in forest floor litter (Table 4.15). The litter layer is a primary receptor of airborne particulate emissions from the smelter. Particulates have accumulated because deposition has occurred much faster than dissolution of the particles. The presence of these particulates in the litter constitutes an extremely unfavorable habitat for invertebrates and other litter-dwelling organisms.

Dissolved metals from the litter layer are free to leach through the litter and into the underlying soil. Metals are then assimilated by plant roots and translocated into above-ground vegetation. Our data indicate that Pb is especially mobile at the 0.4 km site. Values of 334, 2400, 680 and 467 ppm Pb were measured in Al soil, and oak roots, boles and leaves, respectively (Table 4.15). The deposition of highly

Table 4.15. Distribution of Pb, Cd, Zn, and Cu in 6 ecosystem components of Crooked Creek Watershed as a function of distance from the stock.

Distance (km)	Forest-floor litter (g/m <sup>2</sup> )				A1 soil <sup>a</sup> (ppm)				Oak roots <sup>b</sup> (ppm)				Oak boles <sup>c</sup> (ppm)				Oak leaves <sup>d</sup> (ppm)			
	Pb	Cd	Zn	Cu	Pb	Cd	Zn	Cu	Pb	Cd	Zn	Cu	Pb	Cd	Zn	Cu	Pb	Cd	Zn	Cu
0.4	98	0.17	2.8	1.61	334	3.55	25	18	2400	46	48	6.0	680	3.9	30	13	467	3.9	47	10
0.8	28.5	0.07	1.0	0.48	156	1.81	20	10	2.6	1.0	40	9.0	-	-	-	-	-	-	-	-
1.2	13.1	0.04	0.6	0.23	95	0.91	10	3.2	3.6	1.2	33	15.2	-	-	-	-	-	-	-	-
2.0	7.7	0.02	0.4	0.15	-	-	-	-	<6.0	3.7	19	10.1	14	2.4	10	2.2	89	1.9	33	8.5
21 (control)	0.3	0.002	0.07	0.02	13.8	0.23	5.0	0.9	-	-	33	10.0	4.6	0.9	7	1.3	-	-	-	-

<sup>a</sup>1.0 N HCl extraction.

<sup>b</sup>Bark was removed to eliminate surficial contamination.

<sup>c</sup>1974-1970 dated growth ring increments pooled.

<sup>d</sup>Leaf buds were contained in polyethylene bags prior to sampling to eliminate surficial contamination.

soluble Pb particulates on the forest floor, and the low pH (5.5) of forest soil enhance the mobility of Pb in this system.

In general, biological components of the ecosystem are enriched with Cd, Cu and Zn relative to Pb as distance from the smelter increases (Table 4.15). This may be partially due to Cd, Cu and Zn being associated with smaller particulates which are carried further from the stack, and the fact that fugitive Pb concentrate has been deposited at the 0.4 km site.

The quantity of Pb and Cd in spring foliage was estimated by applying the allometric equations for total foliage biomass developed for Walker Branch Watershed<sup>59</sup> (Table 4.16). These values were compared

Table 4.16. Estimated and measured Pb and Cd content of litterfall on Crooked Creek Watershed

Site (km)	Estimated kg/ha		Measured kg/ha	
	Pb	Cd	Pb	Cd
0.4	1.51	0.02	324	0.62
2.0	0.33	0.01	26	0.07

with 01 litter concentrations measured on Crooked Creek Watershed. On the basis of this comparison, leaf uptake of Pb was negligible at the 0.4 km site, and accounted for only 1% of the total Pb content of 01 litter at the 2.0 km site. Particulate loading of Pb on the forest floor apparently overshadows the amount of Pb assimilated by the tree leaves. Foliar uptake of Cd accounted for 3.3 and 12.8% of total Cd content of litter at the 0.4 and 2.0 km sites, respectively. These results indicate 1) Cd is assimilated by trees more readily than Pb, and 2) Cd is less tightly bound in soil; thus, more is available for root uptake.

4.4.3 Effects of Heavy Metals. Ecosystem level effects of smelter emissions on Crooked Creek Watershed documented in this work include (Table 4.17 and Fig. 4.7): 1) accumulation of incompletely decomposed deciduous forest litter out to 2 km from the stack, 2) a disruption of microbial species and populations, 3) depressed macronutrient pools in O<sub>2</sub> litter extending to 0.8 km and an accumulation between 1.2 and 2.0 km, 4) depression of amino sugar content and urease activity as a function of distance from the source, and 5) a depression in cation exchange capacity and pH of litter near the source.

Large accumulations of O<sub>2</sub> litter were measured on Crooked Creek Watershed out to 2.0 km from the smelter stack (Table 4.17). Litter of the O<sub>2</sub> horizon at the 0.4 km site contained a greater mass of fragmented undecomposed leaf material than the control. This accumulation may result from the elimination of arthropod and fungal populations necessary for litter decomposition.<sup>60</sup>

An analysis of litter for amino sugars was utilized to provide insight into the historical microbial and insect activity on the watershed. Amino sugars in litter primarily exist as chitin, which is resistant to degradation and is not synthesized by green plants. Thus, analysis of amino sugars is a specific test for the historical presence of decom-

Table 4.17. Effects of heavy metal contamination on O<sub>2</sub> litter.

Distance (km)	Litter biomass (g/m <sup>2</sup> )	CEC <sup>b</sup> (meq/100 g)	pH <sup>b</sup>	Ca pool <sup>b</sup> (g/m <sup>2</sup> )	Mg pool <sup>b</sup> (g/m <sup>2</sup> )	K pool <sup>b</sup> (g/m <sup>2</sup> )	P pool <sup>b</sup> (g/m <sup>2</sup> )
0.4	1780 <sup>a</sup>	21.1 <sup>a</sup>	4.0 <sup>a</sup>	6.5 <sup>a</sup>	0.98	0.83	0.92
0.8	1921 <sup>a</sup>	19.1 <sup>a</sup>	4.1 <sup>a</sup>	10.9 <sup>a</sup>	1.35	1.31 <sup>a</sup>	0.15 <sup>a</sup>
1.2	1748 <sup>a</sup>	34.9	5.5	22.9	1.64 <sup>a</sup>	1.38 <sup>a</sup>	0.25 <sup>a</sup>
2.0	1595 <sup>a</sup>	33.4	5.2	23.5	1.90 <sup>a</sup>	1.90 <sup>a</sup>	1.08
21 (control)	1008	40.3	5.5	18.5	1.09	0.96	0.80

<sup>a</sup>Significantly different from the control at the 95% level.

<sup>b</sup>Seasonally pooled values (1974).

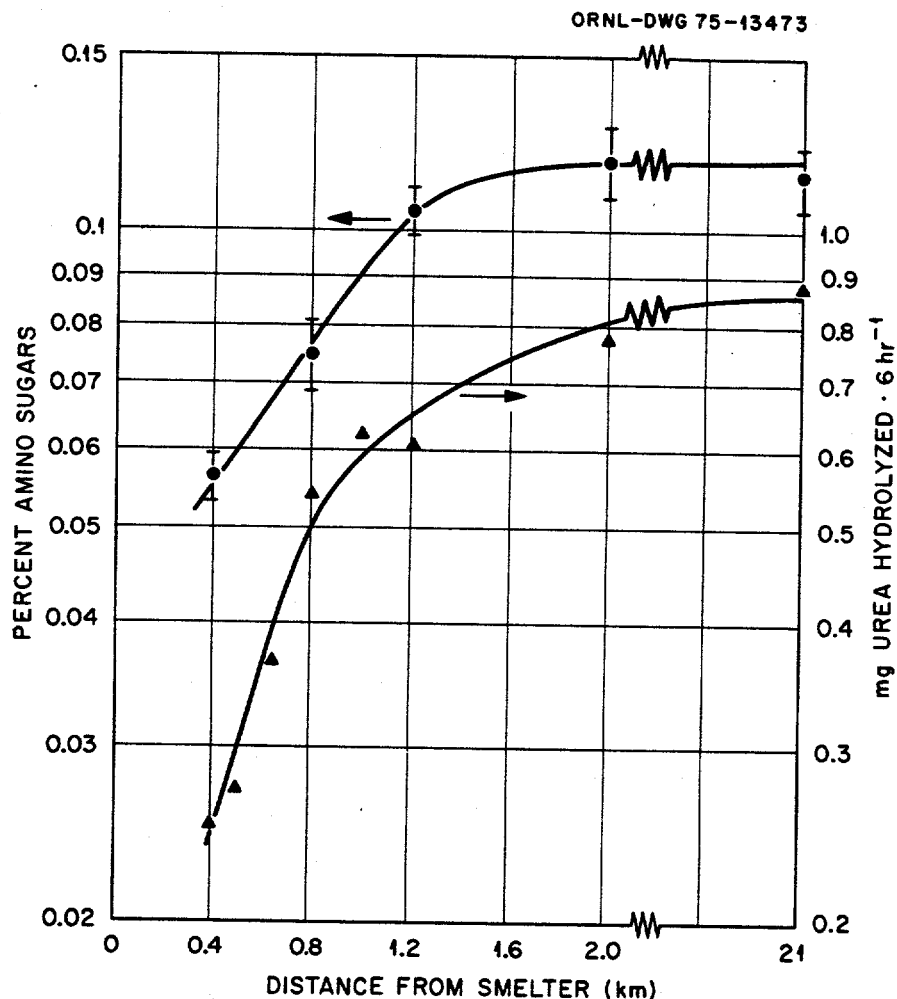


Figure 4.7 Percent amino sugars and urease enzyme activity in litter as a function of distance from the smelter stack on Crooked Creek Watershed.

poser organisms. The result of this test on Crooked Creek Watershed indicates a marked decrease in amino sugars out to 0.8 km from the stack (Fig. 4.7).

Urease enzyme activity in litter was measured to further indicate loss of biological activity on the watershed (Fig. 4.7). This test is more sensitive than the amino sugar assay since the production of urease enzyme is adversely influenced by heavy metal contamination. Laboratory experiments on uncontaminated litter showed that the addition of 10,000

ppm Pb or 800 ppm Zn caused only a 15% reduction in urease enzyme activity. Both metal concentrations and enzyme activity were much higher than that found on the watershed. A reduction of the enzyme activity was found to occur out to 2.0 km from the smelter, which was further than the observed effect on amino sugars. This may indicate that the 2.0 km site is presently being slightly affected by the heavy metal emissions. Thus we conclude that the observed loss of enzyme activity on the watershed is partially due to a depression of microbial activity, and not a simple inhibition of the enzyme.

Populations of fungi and actinomycetes were assessed in Crooked Creek Watershed litter to further document effects on decomposition processes. Dilution plate counts of fungi on rose bengal agar showed no difference between sites on the watershed and the control. The population of actinomycetes, plated on chitin agar, was reduced 100-fold at the 0.4 km site compared to the control. A rare genus, Streptosporangium spp., was found in cultures of litter from the 0.4 km site. The significance of this isolation has not been determined. Further ecological investigations of microbial diversity and populations are warranted to detail the effects of heavy metal emissions.

Coupled with the accumulation of forest floor litter and the depression of microbial processes is a disruption of macronutrient pools in O2 litter (Table 4.17).<sup>61</sup> In general, a depression of macronutrient pools was found out to 0.8 km from the smelter, and an increase out to 2.0 km, relative to the control (21 km). These results were accounted for by a combination of low macronutrient concentrations near the smelter

(0.4-0.8 km), and an accumulation of litter biomass over the entire watershed.

The composition of O2 litter was altered from normal within 0.8 km from the stack. The bulk of O2 biomass was found to be a heterogeneous mixture of coarsely to finely fragmented leaves and twigs with a small amount of humus underlying the leaves. This accounts for the lowered cation exchange capacity of litter within 0.8 km from the stack.

Evidence from this study indicates that heavy metals emitted from the smelter disrupt nutrient cycling mechanisms by initially depressing decomposer activity in litter. This leads to a buildup of forest floor litter; thus, nutrients required for forest production are bound in litter and are not readily available for plant uptake. The net effect is that nutrients from old litter leach out of the system and new litter is deposited which contains increasingly smaller amounts of nutrients. This represents a deterioration of macronutrient cycle and may lead to a loss of forest productivity. We would expect productivity to be most depressed in trees which are intolerant of heavy metals or a reduced supply of available nutrients.

4.4.4 Summary and Conclusions. Further evidence has been obtained in this study to support the hypothesis made by Tyler<sup>62</sup> concerning the impact of heavy metals on forested ecosystems. The essence of the hypothesis is that initial elimination of decomposer populations by metal ions induces an accumulation of incompletely decomposed organic matter. Measured depressions in amino sugar content and urease activity and an accumulation of undecomposed litter on Crooked Creek Watershed support this hypothesis. Continuation of this process forms a destruc-



tive cycle which can affect ecosystem functions, such as macronutrient cycling, and may result in reduced productivity. In extremely severe cases an ecosystem may be completely destroyed.

We hypothesize that the area affected by the smelter is increasing in size due to the continual load of heavy metal particulates on the watershed. The area 1.2-2.0 km from the stack could eventually be affected to the same degree as the existing area within 0.8 km from the stack. The evidence collected in a one-year study of Crooked Creek Watershed supports this hypothesis, but is not adequate to fully test it. Therefore, we recommend that the forest ecosystem on Crooked Creek Watershed be monitored periodically over several years to further assess ecosystem effects. We further suggest that an assessment of macronutrient cycling in an affected ecosystem is important as an indicator of environmental disruption.

#### 4.5 References

1. W. Fulkerson, W. D. Shults, and R. I. Van Hook, Ecology and Analysis of Trace Contaminants Progress Report. ORNL-NSF-EATC-11 (1974).
2. D. S. Bailey, Virginia State Water Quality Control Board Basic Data Bulletin 41:62 (1974).
3. S. G. Hildebrand, J. W. Huckabee, and Y. Talmi, "Total and methyl mercurial levels in benthic invertebrates from a contaminated and uncontaminated stream." In Press. In Proc: International Joint Commission on Great Lakes Research, Duluth, Minnesota (October 6-8, 1975).
4. Tennessee Valley Authority, Mercury in Flesh of Fish Taken from TVA Reservoirs - 1972, TVA special memo report, Chattanooga, Tennessee (1972).
5. Tennessee Valley Authority, Mercury in Flesh of Fish Taken from TVA Reservoirs - 1972, TVA special memo report, Chattanooga, Tennessee (1973).
6. Tennessee Valley Authority, Mercury in Flesh of Fish Taken from TVA Reservoirs - 1973, TVA special memo report, Chattanooga, Tennessee (1974).
7. C. Feldman, ORNL Interlaboratory Procedure for Cold Vapor A. A. S. Analysis for Hg (unpublished). Oak Ridge National Laboratory, Oak Ridge, Tennessee (1972).
8. Y. Talmi, *Analytica Chimica Acta*, 74:107 (1975).
9. Recommended Methods for Water-Data Acquisition, Preliminary report of the Federal Interagency Work Group on Designation of Standards for Water Data Acquisition; impaneled by the U. S. D. I., Geol. Surv., Office of Water Data Coordination (1972).
10. S. Lindberg, "A simple and rapid filtration technique for use with trace element analyses." In preparation (1975).
11. H. Golterman, Methods for Chemical Analysis of Fresh Waters, Blackwell Sci. Publishers, Oxford, England (1969).
12. G. Westöö, *Acta Chem. Scand.*, 20, 2131 (1966).
13. V. Zitko et al., *J. Fish. Res. Board (Canada)* 28, 1285 (1971).
14. W. L. Lockhart et al., *J. Fish Res. Board (Canada)* 29, 1519 (1972).
15. J. W. Huckabee, C. Feldman and Y. Talmi, *Analytica Chimica Acta*, 70:41 (1974).

16. C. A. Bache, W. H. Gutenmann and D. J. Lisk, *Science*, 172:451 (1971).
17. L. R. Kamps, R. Carr and H. Miller, *Bull. Environ. Contam. Toxicol.*, 8:273 (1972).
18. G. Westöö, *Science*, 181:567 (1973).
19. J. H. Bishop and B. P. Neary, pp. III-25, In: Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems. Ottawa, Canada (1974).
20. J. McCarthy, J. Meuschke, W. Flicker, R. Learned, Mercury in the environment. USGS Prof. Paper 713, p. 37 (1970).
21. G. Neville, *Can. Chem. Educ.* 3:4 (1967).
22. D. Johnson and R. Braman, "Distribution of mercury species near ground." *Environ. Sci. Technol.* 8:1003 (1974).
23. W. Lockerety, "Deposition of airborne mercury near point sources." *Water, Air and Soil Pollution* 3:179 (1974).
24. C. Billings and W. Matson, "Mercury emissions from coal combustion." *Science* 176:1232 (1972).
25. S. Lindberg, A. Andren, R. Raridon, and W. Fulkerson, "Mass balance of trace elements in Walker Branch Watershed - the relation to coal-fired steam plants." *Environmental Health Perspectives* (In Press) (1975).
26. M. Berlin, et al. *Arch. Env. Health* 19:891 (1969).
27. L. Friberg, *Nord. Hyg. Tidski* 32:240 (1951).
28. A. Moffitt and R. Kupel, "A rapid method employing impregnated charcoal and atomic absorption spectrophotometry for the determination of Hg." *Am. Ind. Hyg. Assoc. J.* 32:614 (1971).
29. P. Harrison, K. Rahm, R. Dams, J. Robbins, J. Winchester, S. Bras, and D. Nelson, *J. Air Poll. Contr. Assoc.* 21:563 (1971).
30. A. Andren, S. Lindberg, and L. Bate, Atmospheric input and geochemical cycling of selected trace elements in Walker Branch Watershed. ORNL-NSF-EATC-13 (1975).
31. Environmental Protection Agency, National Emission Standards for Hazardous Air Pollutants. Federal Register, Vol. 38, No. 66, p. 8820 (1973).

32. M. Tatsumoto and C. C. Patterson, In: Earth Sciences and Meteorites. J. Geiss and E. D. Goldberg, (Eds.). North-Holland, Amsterdam. p. 74 (1963).
33. K. Bertine and E. D. Goldberg, "Fossil fuel combustion and the major sedimentary cycle." Science, 173, 233 (1971).
34. R. Davis, K. A. Rahn, and J. W. Winchester, "Evaluation of filter materials and impaction surfaces for nondestructive neutron activation analysis of aerosols." Env. Sci. Technol., 6, 441 (1972).
35. W. John, R. Kaifer, and J. Wesolowski, "Trace element concentration in aerosols from the San Francisco Bay area." Atmos. Env., 7, 107 (1973).
36. T. Tanner, J. Young, and J. Cooper, "Multielement analysis of St. Louis aerosols by nondestructive techniques." Chemosphere, 5, 211 (1974).
37. W. McMaster, Hydrologic data for Oak Ridge, Tennessee. Geol. Survey, Water Supply Pap. 1839-N. 60 pp. (1967).
38. D. J. Nelson, "Measurement and sampling of output from watersheds." In: Analysis of Temperate Forest Ecosystems, Vol. 1. D. E. Reichle (Ed.). Springer Verlag, Berlin. 304 pp. (1974).
39. L. N. Peters, D. Grigal, J. Curlin and W. Selvidge, Walker Branch Watershed Project: Chemical, physical, and morphological properties of the soils. ORNL USAEC Rept., ORNL-TM-2968. 89 pp. (1970).
40. J. Elwood and G. S. Henderson, Hydrologic and chemical budgets at Oak Ridge, Tenn. Eastern Deciduous Biome Memo Report # 73-15, 38 pp. (1973).
41. J. N. Galloway and G. E. Likens, "Calibration of collection procedures for the determination of precipitation chemistry." Proc. 1st International Symp. on Acid Precipitation and the Forest Ecosystem (in press) (1975).
42. A. Andren and S. Lindberg, "Atmospheric input and origin of selected elements to Walker Branch Watershed, Oak Ridge, Tennessee." Submitted to Ambio (1975).
43. G. Hoffman and R. Duce, "Copper contamination of atmospheric samples collected with Gelman hurricane hi-vol air samplers." Envir. Sci. Technol. 5:1134 (1971).
44. R. Lee, "The size of suspended particulate matter in air." Science 178:567 (1972).

45. D. Klein and A. Andren, "Atmospheric emissions from coal combustion for power production." *Environ. Sci. Technol.* (In press) (1975).
46. D. Natusch and J. Wallace, "Urban aerosol toxicity: The influence of particle size." *Science* 186:695 (1974).
47. M. Miller, S. Friedlander, and G. Hidy, *J. Coll. Inter. Sci.* 39: 1965 (1972).
48. S. Friedlander, *Environ. Sci. Technol.* 7:235 (1973).
49. R. R. Turner, R. Harriss, T. Burton, and E. Laws, "The effect of urban land use on nutrient and suspended solids export from north Florida watersheds." Proc. Symposium on Mineral Cycling in South-eastern Ecosystems (in press) (1975).
50. A. Taylor, W. Edwards, and E. Simpson, "Nutrients in streams draining woodland and farmland near Coshocton, Ohio." *Water Resour. Res.*, 7, 81 (1971).
51. J. C. Ryden, J. Syers, and R. Harriss, Nutrient enrichment potential of urban soils in the city of Madison. Wisconsin Water Resources Center Techn. Rept., 70 pp. (1972).
52. W. B. Langbein and D. R. Dawdy, Occurrence of dissolved solids in surface waters in the United States. U. S. Geol. Survey Prof. Paper 501-D, p. 115 (1964).
53. Environmental Sciences Division Annual Report, ORNL-4935, 165 pp. (1973).
54. J. D. Hem, Study and interpretation of the chemical characteristics of natural water. U. S. Geol. Survey. Water Supply Paper 1473, 363 pp. (1970).
55. J. J. Jurinak and J. Santillan-Medrano, The chemistry and transport of lead and cadmium in soils. Res. Rept. #18. Agric. Exper. Sta., Utah State Univ., 121 pp. (1974).
56. R. I. Van Hook, W. F. Harris, G. S. Henderson and D. E. Reichle, "Patterns of trace element distribution in a forested watershed." In: Proc. 1st Ann. NSF-RANN Trace Contaminants Conf., Oak Ridge, Tenn. (1973).
57. W. F. Harris, Personal communication.
58. J. Fortescue, D. Burger, B. Grant, E. Gauron, and E. Curtis, Preliminary landscape geochemical studies at forested sites at Dorset, Ontario and Oak Ridge, Tennessee. Progress Report #12, Brook University Dept. Geol. Sci. (1973).

59. P. Sollins, D. E. Reichle and J. S. Olson, Organic matter budget and model for a southern Appalachian liriiodendron forest. EDFB-IBP-73-2. Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830. 150 p. (1973).
60. A. P. Watson, "Trace element impact on forest floor litter in the new lead belt region of southeastern Missouri." In press. Proc. Ninth Annual Conf. on Trace Substances in Environmental Health, Columbia, Mo. (June 9-12, 1975).
61. D. R. Jackson and A. P. Watson, "Disruption of macronutrient pools in forest-floor litter near a lead smelter." Submitted to J. App. Ecol. (1975).
62. G. Tyler, "Heavy metals pollute nature, may reduce productivity." Ambio 1:52 (1972).

## 5. MEASUREMENTS RESEARCH

### 5.1 Introduction

The objective of our measurements research work has been to provide improved analytical methodology that will benefit not only our own research program, but also those of other NSF contractors and those of the scientific community in general (i.e., those that rely upon analytical chemical data). "Improved analytical methodology" implies advances in efficiency and/or capability, as well as the usual performance criteria such as sensitivity, selectivity, and reliability. Our methodology has been and is being implemented within our own laboratories and others, and has spawned a significant number of interactions with workers outside ORNL in addition to numerous publications and oral presentations.

### 5.2 Development of Quantitative X-Ray Fluorescence for Elemental Analysis of Trace Elements in Environmental Samples

C. J. Sparks, Jr.

The objective of this research has been to apply basic understanding of the x-ray fluorescent process so as to advance and improve the capability of XRF for quantitative analysis of trace elements. Increased demands for elemental analysis on a wide variety of samples was caused by the growing concern and interest in environmental monitoring and pollution abatement at trace levels. Much of the analysis was to be performed on samples for which no standards were available and promoted a need for improved x-ray fluorescent methods. More powerful monochromatic x-ray sources were needed to reduce the background under the fluorescent energies to improve the detectability for concentrations

at levels of a few ppm and less. Also, monochromatic sources permit the use of less complicated mathematics to convert the measured fluorescent intensities into concentrations without recourse to the preparation of a range of standard samples to bracket the composition of an unknown sample. More intense monoenergetic sources were obtained from our development of strongly diffracting graphite crystals as a means of selecting a single energy from metal anode x-ray tubes.<sup>1</sup> Improvements were made in the mathematics of using fundamental physical parameters to determine concentrations from measured fluorescent intensities without recourse to preparation of standards.<sup>2</sup> In addition the optical arrangement of the fluorescent instrumentation has been improved through redesign of the collimating slits for the solid state detector.<sup>3</sup> The simplified optics provided for by the use of the energy-sensitive solid state detector permits the use of readily available pure elements and known stoichiometric compounds of widely differing absorption coefficients as standards for many samples of environmental interest.

The highlight of our progress this year has been to clarify the mathematical procedures for applying the "fundamental parameters" approach to converting measured fluorescent intensities to concentrations. We have extended our capabilities to include the effect of interelement enhancement. This provides for more accurate determination of concentrations when other elements are present in excess of 1% producing fluorescent energies capable of exciting excess fluorescence from other elements.

We have also extended the methodology to include quantitative analysis of bulk samples that are too thick for direct measurement of



the absorption coefficients of fluorescent radiations from elements of interest. X-ray fluorescent analysis gives most accurate results when applied to samples in which all elements are in solution. Less ideal samples occur when the elements are separate particles in a mixture. This latter description is the usual case for soils, ores, tailings and geological type samples. We therefore tested the application of the fusion technique<sup>4</sup> of using borate fluxes to dissolve these kinds of samples to form homogeneous solutions, and we have verified the usefulness of the fusion technique for accurate quantitative analysis.

Powerful sources of x radiation are available from electrons circulating in storage rings and synchrotrons.<sup>5</sup> We completed some preliminary experiments to evaluate the application of this intense polychromatic source of radiation to fluorescent analysis at the Stanford Synchrotron Radiation Project, Stanford, California. The radiation is nearly plane polarized with about 90% of the electric vector in the plane of the synchrotron ring. Hence, scattering of the polychromatic source as background under the fluorescent peaks will be a minimum when the detector is placed at 90° to the radiation and in the plane of the synchrotron ring.<sup>6</sup> In comparison to conventional polychromatic sources, synchrotron-radiation-induced fluorescence for the geometry described resulted in a background reduction of about ten. Figure 5.1a shows a fluorescent spectrum taken with polychromatic synchrotron radiation from a sample of fly ash, NBS standard 1633. Electrons circulating at 1.85 GeV, produce photons with energies below about 7 KeV. Thus, the sensitivity is greater for elements emitting fluorescence below this energy. Figure 5.1b was taken with graphite monochromated 17.44 KeV x-rays as

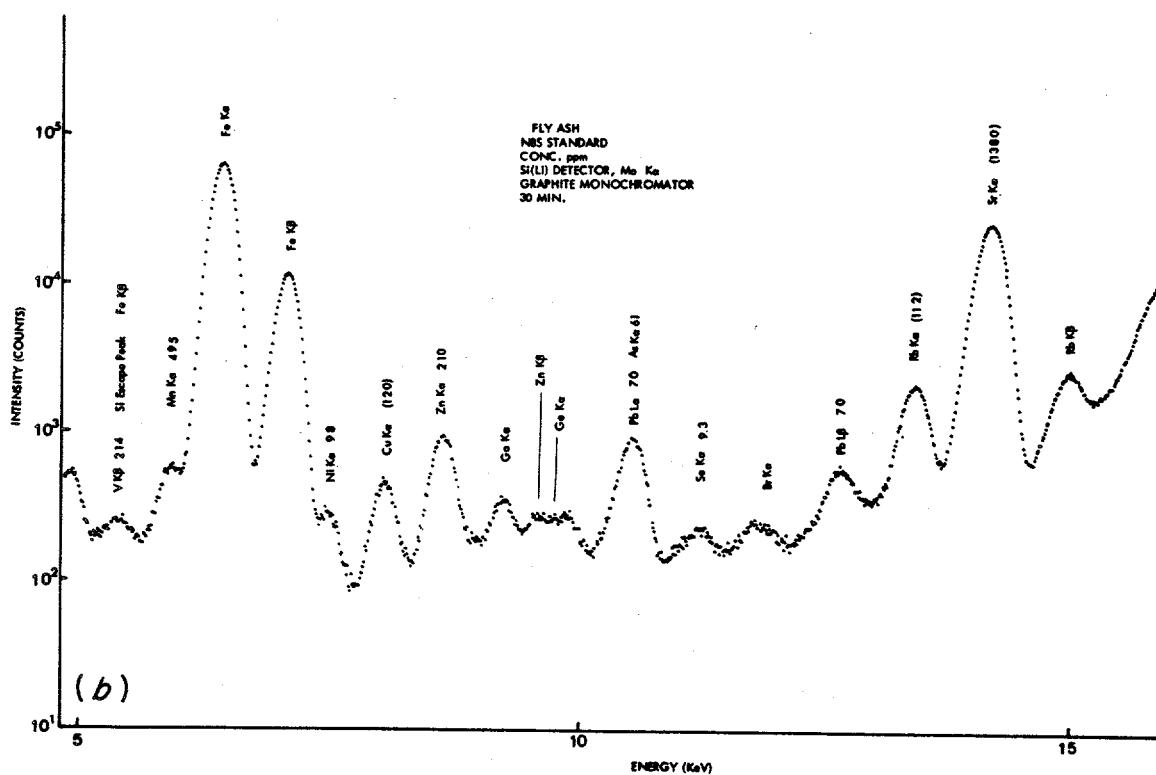
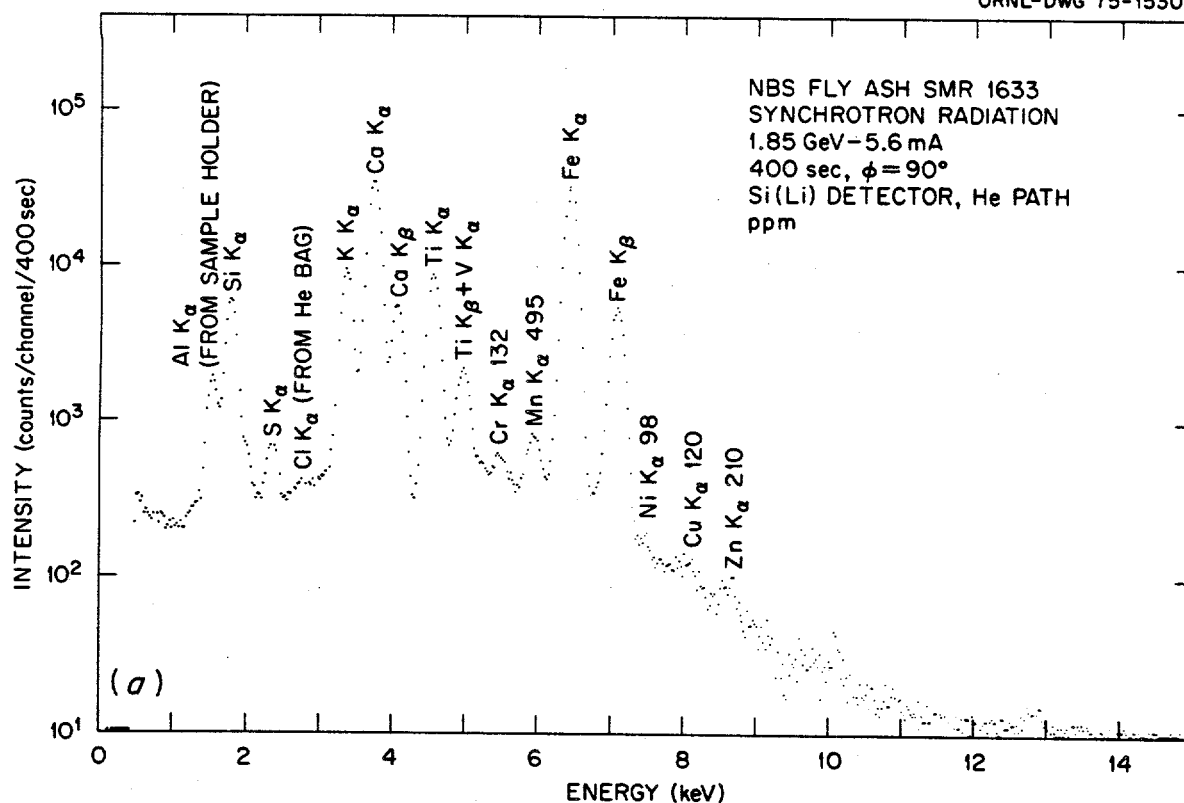


Figure 5.1 Fluorescent spectrum of NBS fly ash SRM 1633 excited by  
a) polychromatic synchrotron radiation, b) monoenergetic source.

the exciting source. We note that the lower energy synchrotron radiation is more efficient in exciting the lower atomic numbered elements. However, the lowest backgrounds and the best signal-to-noise levels are obtained with monoenergetic sources for fluorescence excitation. With the development of fluorescent instrumentation in which the exciting source is monochromated but variable in energy to provide radiation just above the energy of the absorption edge of the elements, detectabilities of a few parts per billion should be attainable.

During this reporting period, considerable effort has been expended to disseminate information on the construction of monochromator mounts, modifications to existing equipment, and assembly of the necessary components for improved x-ray fluorescent instrumentation. Several of our interactions with major X-ray fluorescent instrumentation manufactures occurred because of inquiries from potential customers seeking fluorescent instrumentation containing our innovations. Some of the more significant interactions with others are the following. Drs. Stan Bates, Frank Blanchard and R. W. Gould of the University of Florida have constructed a fluorescent unit duplicating the essential features of our unit for the analysis of geological and environmental samples associated with the minerals industry in the state of Florida. Dr. Thomas C. Furnas, President, Molecular Data Corp., Cleveland, Ohio, was given information on design and construction of monochromators. This small instruments company supplies consulting services and instrumentation for x-ray fluorescent and diffraction equipment. It is presently developing monochromators and mountings for such equipment. Dr. Charles Miller, Department of Physics, Anderson College, Anderson, Indiana

has received a NSF Instructional Equipment Grant which includes \$20,000 for x-ray fluorescent equipment. We have supplied him with information about the ORNL-developed fluorescent unit and consulted about equipment purchase. Their fluorescent unit will be used both in research on problems of environmental concern and for instructional training of students. Dr. Lee Middleman, Nuclear Semiconductor, Menlo Park, California and Dr. Dale Gedcke and Don Bartell, ORTEC, Oak Ridge, Tennessee have continued to receive information on detector design changes, graphite monochromators and thin graphite windows for detectors. Both companies are major manufacturers of energy sensitive detectors and fluorescent instrumentation and have adapted several of our design changes. A. L. Coffey, Jr., regional sales manager for Diano Corp., Nashville, Tennessee (a major manufacturer of wavelength dispersive fluorescent equipment) has asked us for information for modifying their equipment because of customer inquiries prompted by our work. We have continued to work with Norma Bottone, Dr. Arthur Moore and Donald Mentzer of Carbon Products Division of Union Carbide Corporation. As UCC is the sole manufacturer of these high efficiency monochromators, we have kept them informed on the specifications necessary to supply the needs of the fluorescent users. We have run samples for Dr. R. D. Irons, Department of Pathology, Pharmacology and Toxicology, School of Medicine and Dentistry, Rochester, N. Y., for trace elements in mammalian organs as part of his evaluation of analytical techniques. Drawings for the attachment of a monochromator to a G. E. XRD-3 spectrogoniometer were sent to John Kuhns and Rodney Ruch of the Illinois State Geological Survey, Champagne, Illinois.

The significance of this work is that we have provided an improved analytical technique for multielement analysis at the parts per million level, with broad application to the analytical needs of environmental monitoring and pollution abatement activities. In comparison with other analytical techniques, this improved x-ray fluorescence method is relatively inexpensive, provides rapid quantitative analysis and will greatly increase the analytical capability for environmental analysis at the trace concentration level.

### 5.3 Development and Application of Multi-Element Isotope Dilution

#### Spark-Source Mass Spectrometry and Ion Microprobe Mass Spectrometric Techniques for Environmental Samples J. A. Carter<sup>a</sup>,

W. H. Christie, D. L. Donohue, J. C. Franklin, D. H. Smith and  
R. W. Stelzner

The two main objectives of this study have been: 1) to develop semiquantitative multi-elemental spark source mass spectrometry (SSMS) into a quantitative technique by establishing multi-element isotope dilution (ID) methodology, and 2) to investigate isotope dilution as a means for quantifying ion microprobe mass analysis (IMMA). These objectives required the accomplishment of several specific tasks. Studies of the equilibrium between spike and sample isotopes and of optimum spectrometer conditions were required. It was necessary to develop an interactive data system for interpretation of data from SSMS photoplates. Additionally, testing and direct application of multielement spiking was needed, using a variety of sample types. For IMMA, the installation and

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<sup>a</sup>Task Leader.

checkout of the instrument had to be done and surface profiling studies were necessary. Quantification of data and application of ID methods to samples, using IMMA, are desirable but have not been completed within the short duration of this project.

The data acquisition system for the SSMS photographic plates is essentially complete.<sup>7,8</sup> A PDP-8 computer acquires data from the photoplate, converts percent transmittance (% T) to intensity, and corrects for background on either side of the measured lines. The computer then calculates elemental concentration using the mathematics of isotope dilution, or prepares a paper tape of intensity data and elemental identification for further processing. The precision of the data system and emulsion calibration is such that the % T of any line can be converted to ion intensity with a relative standard deviation of less than 2%. For convenience of data output when measuring several elements, we are presently preparing the PDP-8 data system to collect data and calculate and output isotope dilution data with an IBM 1130 computer system.

The multi-element isotope dilution method has been successfully applied to the analysis of gasoline, gasoline additives, fuel oil, and water samples.<sup>9-11</sup> The most fundamental requirement of isotope dilution is that chemical equilibrium between the spike and sample isotopes be obtained. If the materials to be analyzed are non-organic, such as water or alloys, this equilibrium is almost invariably obtained in the process of dissolution and extraction of the sample. The analysis of organic materials such as gasoline, solvents, coal, fuel oils, and tissue present difficult problems of equilibration. The metallic impurities in organic materials are present as unknown organo-metallic compounds.

The isolation and identification of these organo-metallic compounds is not practical at the sub-microgram level. This problem is compounded by the fact that the enriched stable isotopes used as spikes are available as pure elements or oxides and have been prepared in acid solutions.

Various methods of equilibration were investigated. Initial work with organic samples included oxidation with bromine which produced a viscous tar that was freeze dried and then heated in vacuum at 60° C. The product of this process was a carbon residue which was pressed and sparked. This method of sample preparation was not reproducible; the spike or standard was added in all cases prior to the oxidation, yet recovery of the spike or standard was often erratic.

Wet oxidation of gasoline was attempted on samples with internal standards added, but the oxidation was so vigorous that process blanks were difficult to evaluate. Extraction of the metals into aqueous acids was attempted, and for specific elements this process was satisfactory. Enriched isotopes of a few elements are easily recovered, but the extractions were not satisfactory for surveying a large number of elements.

The method now used for gasoline requires that the spike isotopes be added to one ml of HCl. Ten ml of gasoline are added to the HCl spike solution; the two-phase system is refluxed for 4-6 hours. The aqueous phase is removed, dried on graphite electrodes and sparked. To confirm the technique, synthetic samples were made from alkyl metal sulfonates obtained from Continental Oil Company and from NBS organo-metallic standard reference materials. The recovery rate for most metallic elements in the synthetic samples is greater than 80% by the reflux method. The precision at the  $0.5 - 1 \times 10^{-6}$  g/ml level is about

10%. Gasoline samples have been analyzed for 26 elements at concentration levels between  $1 \times 10^{-9}$  g/ml and  $1 \times 10^{-6}$  g/ml. Mononuclidic elements such as bismuth were determined using isotopes of other elements as internal standards. Analysis of fuel oil and gasoline additives was accomplished by wet ashing the sample in  $\text{HClO}_4/\text{HNO}_3$  followed by addition of the spike mixture. The spiked solution was dried on graphite electrodes and sparked.

Isotope dilution techniques have been employed for the analysis of distilled water, tap water, and stream waters. A spike solution consisting of eleven enriched isotopes ( $^{204}\text{Pb}$ ,  $^{196}\text{Hg}$ ,  $^{183}\text{W}$ ,  $^{106}\text{Cd}$ ,  $^{97}\text{Mo}$ ,  $^{77}\text{Se}$ ,  $^{67}\text{Zn}$ ,  $^{65}\text{Ca}$ ,  $^{61}\text{Ni}$ ,  $^{57}\text{Fe}$ ,  $^{53}\text{Cr}$ ) and isotopically normal erbium has been prepared for use with water samples. Mononuclidic elements such as As and Co were compared with the enriched isotope that is nearest in mass; i.e.,  $^{75}\text{As}$  is compared with  $^{77}\text{Se}$ .

Detection limits for impurities in water are functions of the volume that has been preconcentrated. The sample volume in this work has been 100 ml, sufficient to provide detection limits in the range of  $5 \times 10^{-11}$  g/ml. Waters with high mineral content leave a complex residue on the electrodes and may raise the detection limit by a factor of 10 for some elements. Our isotope dilution studies have also aided in the determination of relative sensitivity factors which are useful in routine survey analysis.

To summarize, spark source mass spectrometry, using isotope dilution techniques, has been shown to be an accurate and precise method of analysis for trace level impurities in a wide variety of sample types. The method has been successfully employed in the analysis of water,



dust, gasoline,  $^{233}\text{UO}_2$ , fuel oils, animal tissues, cigarette tars, and various alloys. Impurity concentrations have been accurately and precisely determined at concentration levels between  $5 \times 10^{-11}$  g/ml and  $10^{-4}$  g/ml. In general, if  $1 \times 10^{-9}$  g of an element and a spike isotope can be placed on the electrode, its concentration can be determined with a precision and relative error of less than 10%. This multi-element isotope dilution analysis technique adds new dimensions of precision and accuracy to the high sensitivity and broad elemental coverage of spark source mass spectrometry.

Our work with the ion microprobe mass analyzer was originally scheduled to begin in July, 1975 and continue for twelve months. The work was initiated earlier because of the condensed duration of the program, and much remains to be done. Considerable effort has been put into the quantification of IMMA data.

Two approaches have been used to attack the quantification problem; both necessitate the use of a computer to process the data. The first method, developed by Andersen,<sup>12</sup> involves the assumption of local thermal equilibrium (LTE) and the use of the Saha-Eggert equation. The program tests an array of temperatures and electron density values for the minimum in the error function of one or two internal standards. Even though the underlying assumptions are not universally accepted, the model has had some success. We have had CARISMA, the proprietary Applied Research Laboratories' program, set up on an IBM 360 computer. We have also stored an altered version of a simplified LTE model on our own IBM 1130 computer.<sup>13</sup> In this program, corrections for the formation of negative ions and doubly charged positive ions are neglected.

The NBS 660 series of steel standards were analyzed, and elemental concentrations obtained by CARISMA and by the modified program were compared. The differences between the two programs were not great considering the overall accuracy of the LTE approach. In general, either program calculated metals with an accuracy of a factor of 2 (Mo was an exception) for concentrations less than 1%. The programs failed completely for non-metallic and semi-metallic elements such as arsenic.

The second approach, based upon the use of sensitivity factors, is similar to the technique that has been used successfully in spark source mass spectrometry for some years.<sup>14-16</sup> The major complicating factor in applying this technique to IMMA is that data are sensitive to the sample matrix. Therefore, the composition of a standard must be very similar to that of the sample. Probe standards are not yet common, but a simple determination of sensitivity factors from the NBS-660 suite of iron standards indicates that this approach merits further investigation.

Some work has been done on NBS glass standards, and the results indicate that reasonable data can be obtained. One of the problems involved in the analysis of non-conducting samples is the buildup of surface charge during bombardment with positive ions. Unless prevented, the resulting instabilities in the ion optics of the system preclude reliable collection of data. A negative primary ion beam is usually successful in controlling instability, but results in a significant loss of sensitivity for electropositive elements. Frequently charge buildup can be prevented by application of a thin film of carbon, but this technique is not uniformly successful. To improve our sample handling flexibility, we installed an electron gun in the sample chamber of the

IMMA instrument. The electron beam successfully neutralized excess positive charge and allowed us to study samples that would have caused problems, e.g., the leaf described below. An improved version of the electron gun is in the design stage and will be installed later.

A leaf from the vicinity of a lead smelter was analyzed and the surface distribution of K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Cd, and Pb was determined. Ion micrographs showed the presence of Pb in all particles; the other elements were not present in all particles. Spark source mass spectrometric analysis by isotope dilution gave the following concentrations: Cd, 0.57; Cu, 3.5; Zn, 9.8; Pb, 75  $\mu\text{g}/\text{cm}^2$ .<sup>2</sup> The question of the chemical state of Pb on such samples is important because it will determine the ease with which the Pb enters an ecosystem. Although IMMA gives no direct information on chemical form, it is possible to make inferences from the presence or absence of certain masses in the spectrum. Since Pb was shown to be present on the leaf, a differentiation between PbS or PbSO<sub>4</sub> was desired. A primary ion beam of Ar<sup>+</sup> was used to allow investigation of oxygen and sulfur distribution, and negative ions were monitored to enhance our sensitivity for electronegative molecular species. A series of ion micrographs, all showing the same spatial distribution, was made at the following masses: 96(SO<sub>4</sub><sup>-</sup>); 208(Pb<sup>-</sup>); 224(PbO<sup>-</sup>); 240(PbO<sub>2</sub>; PbS<sup>-</sup>); 256(PbO<sub>2</sub><sup>-</sup>; PbSO<sup>-</sup>); 272(PbO<sub>4</sub><sup>-</sup>; PbSO<sub>2</sub><sup>-</sup>); 288(PbSO<sub>3</sub><sup>-</sup>); 304(PbSO<sub>4</sub><sup>-</sup>). The presence of the higher masses (288 and 304) is strong evidence for the presence of PbSO<sub>4</sub>. Since lead sulfide ions and a series of lead oxide ions would be expected to form from PbSO<sub>4</sub>, nothing can be said concerning the presence or absence of PbS and PbO on the leaf.

A number of studies were carried out to investigate the applicability of the multi-element spiking technique to IMMA. A suitable substrate for solutions was found to be pyrolytic graphite, which did not absorb the sample, as Cu and pressed graphite did. Unfortunately, due to the differing solubilities of the various elements, it was not possible to obtain a uniform distribution of them on the surface. The solutions were loaded as one-microliter drops on the pyrolytic graphite surface. As the drop evaporated and contracted, less soluble species precipitated out of the solution first and the more soluble species precipitated last. Thus, while it was quite easy to obtain a signal for each element, the composite of any one area was no longer representative of the solution as a whole. The quantity of a given element in the solution could still be obtained by measuring the ratio of one of its natural isotopes to the spike isotope. We were able to determine Zr concentration in a solution containing about 0.2 ng Zr with a precision of 10% relative standard deviation.

Summarizing, our work thus far indicates that IMMA data can only be made semi-quantitative; more work is needed to improve results, but it is doubtful that truly quantitative IMMA data can be obtained in the near future. IMMA is unsurpassed, however, in its ability to present spatial distribution data for a wide range of elements.

#### 5.4 Gas Chromatography Research D. A. Bostick, C. Feldman, W. H.

Griest, M. R. Guerin<sup>a</sup>, C. H. Ho, A. D. Horton, and Y. Talmi<sup>a</sup>

The objectives of this work have been 1) to develop gas chromatography with microwave excited spectrometric detection (GC/MES) as a

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<sup>a</sup>Task Leaders.

technique for performing difficult analytical measurements of environmental significance and 2) to develop and apply advanced gas chromatographic techniques to the characterization of materials derived from fossil fuels. Major accomplishments of this report period include a) the development of a method allowing part per trillion determinations of  $\text{CH}_3\text{HgCl}$  in waters, b) development of a method for determining alkyl-arsenic acids, c) demonstration of the utility of GC/MES for selectively identifying and quantitating silicon-containing compounds, d) demonstration of the practicality of multicomponent GLC profiling of polynuclear aromatic hydrocarbons in complex fossil fuel samples, and e) finding that the combination of fractionation and gas chromatographic profiling is particularly suited to characterizing coal-derived samples. Y. Talmi, D. A. Bostick, and C. Feldman have been responsible for GC/MES developments. M. R. Guerin, W. H. Griest, C. H. Ho, and A. D. Horton have been responsible for extending existing gas chromatographic capabilities to coal-related samples.

Because of its inherent sensitivity and selectivity, the GC/MES has proved a versatile tool in the analysis of volatile non-metal and organo-metallic species. For the past three years, the GC/MES has been routinely applied to the determination of volatile mercury compounds. Using the MES detector system, levels from 0.002 to 0.0005 ng of mercury have been determined with a selectivity of greater than 10,000 in such complex matrices as biological tissues and sediment samples. The relative sensitivities obtained for  $\text{CH}_3\text{HgCl}$  in natural waste waters are improved by preconcentrating the contaminant from large sample volumes.<sup>17</sup> Previous studies have demonstrated the excellent extractability of

inorganic anionic complexes of mercury, from alkaline as well as acidic solutions, with quarternary amines dissolved in various organic solvents. We have continued these studies and found that tertiary amines are even more efficient in extracting  $\text{CH}_3\text{HgCl}$ . With 0.5% tertiary-amine benzene solutions, a quantitative extraction of  $\text{CH}_3\text{HgCl}$  ( $95 \pm 3\%$ ) can be achieved for (aqueous)/(solvent) volume ratios as high as 400. Following extraction, 1-10  $\mu\text{l}$  aliquots of the benzene extract are injected into the gas chromatograph for analysis. In the injection port ( $200^\circ \text{C}$ ), the  $\text{CH}_3\text{HgCl}$ -amine complex is instantly cleaved to release the volatile  $\text{CH}_3\text{HgCl}$  which is then separated by the GC column in exactly the same manner as pure  $\text{CH}_3\text{HgCl}$  standards. Using this analytical technique, trace  $\text{CH}_3\text{HgCl}$  as low as 1 ng/l can be determined in water samples with an accuracy and precision of 10-15%. The excellent sensitivity and relative simplicity of this analytical technique is of considerable interest to environmentalists who are concerned with the mechanisms of  $\text{CH}_3\text{HgCl}$  accumulation in various biological systems.

The GC/MES has also been applied to the analysis of alkylarsenic acids in industrial pesticide and environmental samples.<sup>18,19</sup> Previous analytical techniques have generally relied on the determination of total arsenic content to monitor the impact of arsenic in the environment. However, there is now evidence that the bioaccumulation of certain alkylarsenic herbicides also occurs in the environment. In addition, organoarsenic acids have been shown to undergo reduction by microorganisms to toxic and volatile arsines. Therefore, to study the true history of arsenic herbicides in the environment, an accurate and sensitive analytical technique is required which is capable of providing

information concerning the chemical form of the arsenicals, in addition to their arsenic content. Our new procedure involves a  $\text{NaBH}_4$  reduction of alkylarsenic acids, particularly mono- and dimethylarsenic acids, contained in acidic aqueous samples to their corresponding alkylarsines. The gaseous arsines are collected by either of two methods: a) extraction of the gases with toluene or benzene concurrently with  $\text{NaBH}_4$  reduction of the acids, or b) flushed, through the effervescence of the  $\text{NaBH}_4$  reduction reaction, into a cold toluene trap ( $-5^\circ \text{C}$ ). The arsine collection procedure employed depends upon the volatility of the alkylarsine generated. Highly volatile monomethylarsine was collected using the toluene cold trap. Dimethylarsine was collected using both procedures. Because of their low volatility, alkylarsines possessing greater than a two-carbon organic moiety could only be collected efficiently by the extraction technique. Aliquots of the organic phase, using either collection procedure, were subsequently injected into and separated by a GC column. The separated alkylarsines were eluted into an argon plasma where they were detected by monitoring the  $2288 \text{ \AA}$  As emission line. Using the cold toluene trap procedure, linear working curves were obtained for both mono- and dimethylarsenic acid in the 0.03 - 100 ng range. This corresponds to a relative sensitivity of 0.01  $\mu\text{g/ml}$  alkylarsenic acids in water samples. By preconcentrating the alkylarsines evolved from large sample volumes into a minimum volume of toluene, the relative sensitivity can be reduced by at least a factor of 40. With this extended range, the present analytical method can be used to separate and individually determine alkylarsenic acids as either major, minor or trace sample components.

In a further study, the GC/MES was adapted as a silicon selective detector that will be used to aid in the characterization of the numerous organic compounds eluted during the GC separation of coal-derived effluents. With this adaptation, those compounds containing active hydrogen atoms can be identified in the presence of other volatile components as silyl derivatives. Silicon detection has been investigated using both a helium and an argon plasma. The spectral characteristics of silicon in a helium plasma were studied by measuring the emission intensity of the silanizing reagent, bis(trimethylsilyl)trifluoroacetamide (BSTFA), in benzene. Monitoring the  $2516.1 \text{ \AA}$  Si emission line, BSTFA could be detected in the 10-1000 ppm concentration range. However, under optimum conditions, the best selectivity for silicon, when compared to a non-silicon containing compound was 25. The reproducibility in analyzing a sample was very dependent upon the ability to control both the power of the plasma and the duration of the silicon-containing compound in the plasma. In an effort to reduce the influence of these factors on silicon determination, the less energetic argon plasma was used. The plasma was operated both in vacuum (5-10 Torr) and at atmospheric pressure. Monitoring several Si atomic emission lines, the best silicon response occurred at the  $2516 \text{ \AA}$  Si line in vacuum. Silicon selectivity and sensitivity varied with the region of the plasma monitored; both parameters being a maximum when Si response was detected in the extreme upstream portion of the plasma. In contrast to the helium plasma, sensitivity and reproducibility were only slightly dependent upon microwave power. When the above parameters are optimized, the detection limit of the silanizing reagent samples is 0.1-100 ppm with a reproducibility of



2-3% and selectivity greater than 250. In our final studies, real samples will be used to evaluate the usefulness of the GC/MES for determining silanized compounds.

Element selective detection gas chromatography has also proven useful in studies of coal-derived samples for the sulfur-bearing constituents. A commercial flame photometric detector set to monitor sulfur has been used to locate the sulfur-bearing fraction of coal-derived products and to analyze gaseous effluents. One stack gas sample was found to contain  $\text{H}_2\text{S}$  and COS at concentrations of at least 10 ng/ml. Considering the bag sampling technique used and the age of the sample, we feel that original concentrations were much higher. Hydrogen sulfide in particular is known to react with organic constituents in such samples.

Sulfur-containing constituents of synthetic crude oils are extremely important for environmental and health reasons. Figure 5.2

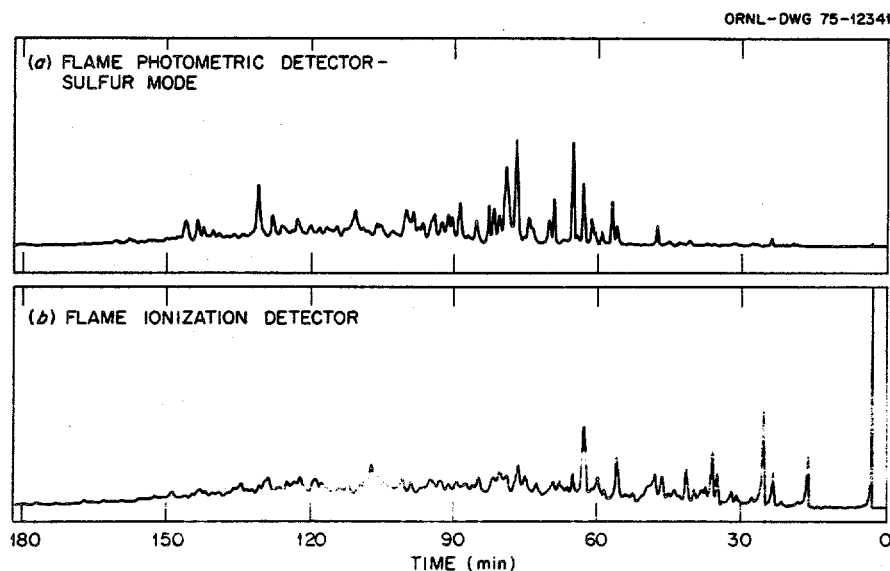


Figure 5.2 Gas chromatographic analysis of a synthetic crude oil fraction distilling from  $55^\circ$  to  $176^\circ$  C/1mm Hg. a) Flame photometric sulfur-selective detector,  $256 \times 10^3$  attenuation, b) flame ionization detector,  $256 \times 10^2$  attenuation.

illustrates the complexity of the sulfur components as determined by profiling a boiling point fraction. Positive identification of the constituents is complicated by the inapplicability of direct GC-mass spectrometry; organics free of sulfur are visualized as interfering impurities in the mass spectrum. We find that the sulfur component can be enriched by preparing an aromatic-rich subfraction of the neutral fraction of coal liquids. The constituents can then be purified by thin layer chromatography prior to GC-MS identification. Selective trapping of vapor phase sulfur constituents using mercury salts affords a convenient means of preparing such samples for identification.

Quantitative determinations of polynuclear aromatic hydrocarbons (PAH) also require extensive pre-separation. Our routinely employed method for the determination of phenanthrene, benz(a)anthracene (BaA), and benzo(a)pyrene (BaP) involves serial extractions to prepare a PAH-enriched subfraction, florisil column cleanup, alumina column separation by ring number, paper chromatographic or acetylated cellulose column chromatographic purification of BaA and BaP, and finally gas chromatographic or fluorometric measurement. Isotope dilution must be used to determine recoveries. We find that it is possible to collect the 2-7 ring PAH constituents from the alumina column and subject the entire fraction to gas chromatographic analysis.

Figure 5.3 illustrates the chromatograms obtained with a known mixture, the PAH isolate from a condensed cigarette smoke, and the isolate from a coal-liquefaction product. Table 5.1 identifies the peaks and presents results found for one liquefaction product. The coal-derived material contains PAH's at concentrations of from 10-100

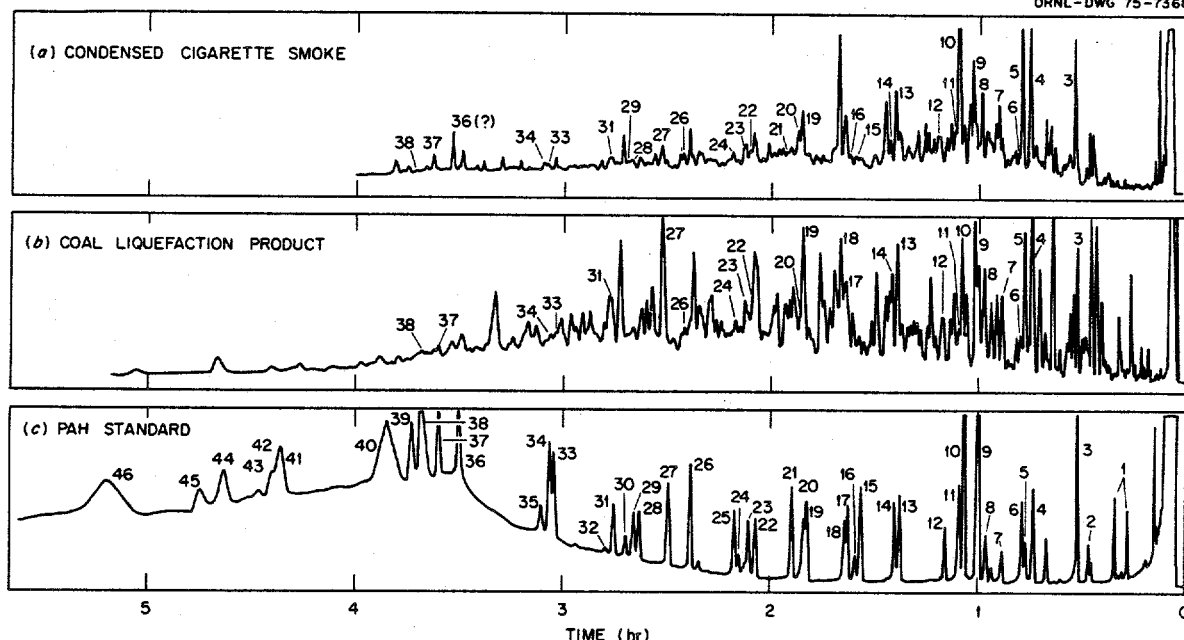


Figure 5.3 Gas Chromatograms of PAH-enriched subfractions. a) Condensed tobacco smoke, 8 x 10 detector attenuation, b) coal liquefaction product, 64 x 10, c) PAH standard.

times that in condensed tobacco smoke. Considering that the condensate shown is carcinogenic in the mouse skin model and that the PAH content of the condensate is largely responsible for the bioactivity, we would predict a very significant carcinogenicity for the coal-derived liquid tested in the same model. Additional development is underway to improve the resolution of lower molecular weight PAH's and to improve recoveries. Recoveries of 90-100% and resolution of most of the major constituents is possible.

Capillary column gas chromatography, particularly when combined with cryothermal temperature programming, is found to be an excellent tool to visualize organic constituents in stack gas and headspace samples. We observe at least 50 low molecular weight compounds by transferring sample from the collection bag to the head of a 150' stain-

Table 5.1. PAH profile peak identifications and quantities of selected constituents a coal-derived liquid.

Peak No.	PAH
1	cis-and trans-Decahydronaphthalene
2	1,4-Dihydronaphthalene
3	Naphthalene (347) <sup>a</sup>
4	2-Methylnaphthalene (1325)
5	1-Methylnaphthalene (383)
6	Azulene
7	Biphenyl (89)
8	2,6-Dimethylnaphthalene (328)
9	1,3-Dimethylnaphthalene (181)
10	Butylated hydroxytoluene
11	Acenaphthalene (20)
12	Acenaphthene (61)
13	Fluorene (205)
14	9,10-Dihydroanthracene
15	9-Methylfluorene
16	9,10-Dihydrophenanthrene
17	Octanthrene
18	1-Methylfluorene (152)
19	Phenanthrene + 1,3,6-Trimethylnaphthalene (Phen, 413)
20	Anthracene
21	1-Phenylnaphthalene
22	2-Methylantracene
23	1-Methylphenanthrene (107)
24	2-Phenylnaphthalene
25	9-Methylantracene (42)
26	Fluoranthene
27	Pyrene
28	1,2-Benzofluorene
29	2,3-Benzofluorene
30	4-Methylpyrene
31	1-Methylpyrene
32	5,12-Dihydrotetracene
33	1,2-Benzanthracene (BaA, 18)
34	Chrysene + Triphenylene (Chry, 98)
35	2,3 Benzantracene
36	7,12-Dimethylbenz(a)anthracene
37	Triphenylbenzene
38	1,2- + 3,4-Benzopyrene (BaP, 41)
39	Perylene
40	Impurity + 3-Methylcholanthrene
41	1,2,5,6- + 1,2,3,4-Dibenzanthracene
42	o-Phenylenepyrene
43	Picene
44	1,12-Benzoperylene
45	Anthanthrene
46	3,4,9,10-Dibenzopyrene + Coronene

<sup>a</sup>Concentration in ppm found in one coal derived liquid product.

less steel capillary column packed with a 1:2 ratio of Ucon LB-550X and Ucon HB-280X cooled to 0° C, then programmed to 110° C at 1° C/min. Warming a coal liquid to 50° C and transferring the volatiles to the same analytical system reveals at least 75 constituents. These "vola-

tiles" may be representative of in-plant fugitive emissions in the absence of safeguards. Efforts are now underway to construct glass capillary columns to take advantage of its lower surface activity and allow the use of a greater variety of coatings. The combination of pre-fractionation, cryothermal programming, glass capillary columns, and the MES detector constitutes an analytical methodology of general applicability and major significance. This methodology should be useful in a variety of programs that are concerned with organic contaminants.

#### 5.5 Liquid Chromatography Research R. L. Jolley and W. W. Pitt, Jr.<sup>a</sup>

The overall objective of this project has been to apply high-resolution liquid chromatography to the characterization of the organic materials in natural and polluted waters including the aqueous effluents from coal-conversion processes. During this report period preliminary studies were made with water samples from a large metropolis, from an algae culture, and from an estuary; several aqueous effluents from a coal-conversion plant were investigated; and a chlorinated cooling water sample from an electric-power plant was analyzed. In addition the chromatographic separation and analytical procedure for phenolic compounds was optimized to facilitate the analysis of coal-related effluents.

Because of the high probability of coal becoming the major energy source in the near future and the consequent utilization of coal for the production of gaseous and liquid fuels, coal-related waste effluents may become environmentally significant. The application of high-pressure liquid chromatography (HPLC) to the determination of non-volatile organic

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<sup>a</sup>Task Leader.

constituents in aqueous effluents from coal-processing plants as previously reported,<sup>20</sup> has continued. In addition to samples from two aqueous streams from a coal-char oil process, a sample from a hydrocarbonization experiment was analyzed by HPLC. All samples were chromatographed without prior concentration and each chromatogram showed many uv-absorbing and cerate oxidizable constituents (Fig. 5.4). Over 80 uv-absorbing compounds were separated by preparative-scale chromatography of the product separator sample. Using a multicomponent analytical identification and quantitation procedure,<sup>21</sup> six phenolic compounds were identified and quantified (Table 5.2) and 12 were characterized with respect to their gas chromatographic and mass spectral properties. Methylene chloride extracts were made on both samples from the coal-char oil process. Using combined gas chromatography-mass spectrometry, dioctylphthalate was found to be the single major component of the off-gas scrubber sample. In the more complex product separator sample, phenol, three cresols, three dimethylphenols, and xylene were identified and seven other unknowns were characterized.

Table 5.2. Soluble organic constituents in the aqueous product separator sample from a coal-char oil conversion plant.

Constituent	Concentration (mg/liter)			
	FID <sup>a</sup>	Enzyme <sup>b</sup>	Prep. AC <sup>c</sup>	Anal. AC <sup>d</sup>
Catechol	660	560	>3,600	2,000
3-Methylcatechol	170			
4-Methylcatechol	110			
Orcinol	120		380	500
Resorcinol	220		790	1,000
2-Methylresorcinol	14		100	10-50

<sup>a</sup>Based on Flame Ionization Detector response during gas chromatography.

<sup>b</sup>Analyzed by B. Z. Egan using a catechol specific enzyme technique.

<sup>c</sup>Based on the uv-absorbance of the preparative-scale chromatographic peak.

<sup>d</sup>Based on the uv-absorbance of the analytical-scale chromatographic peak.

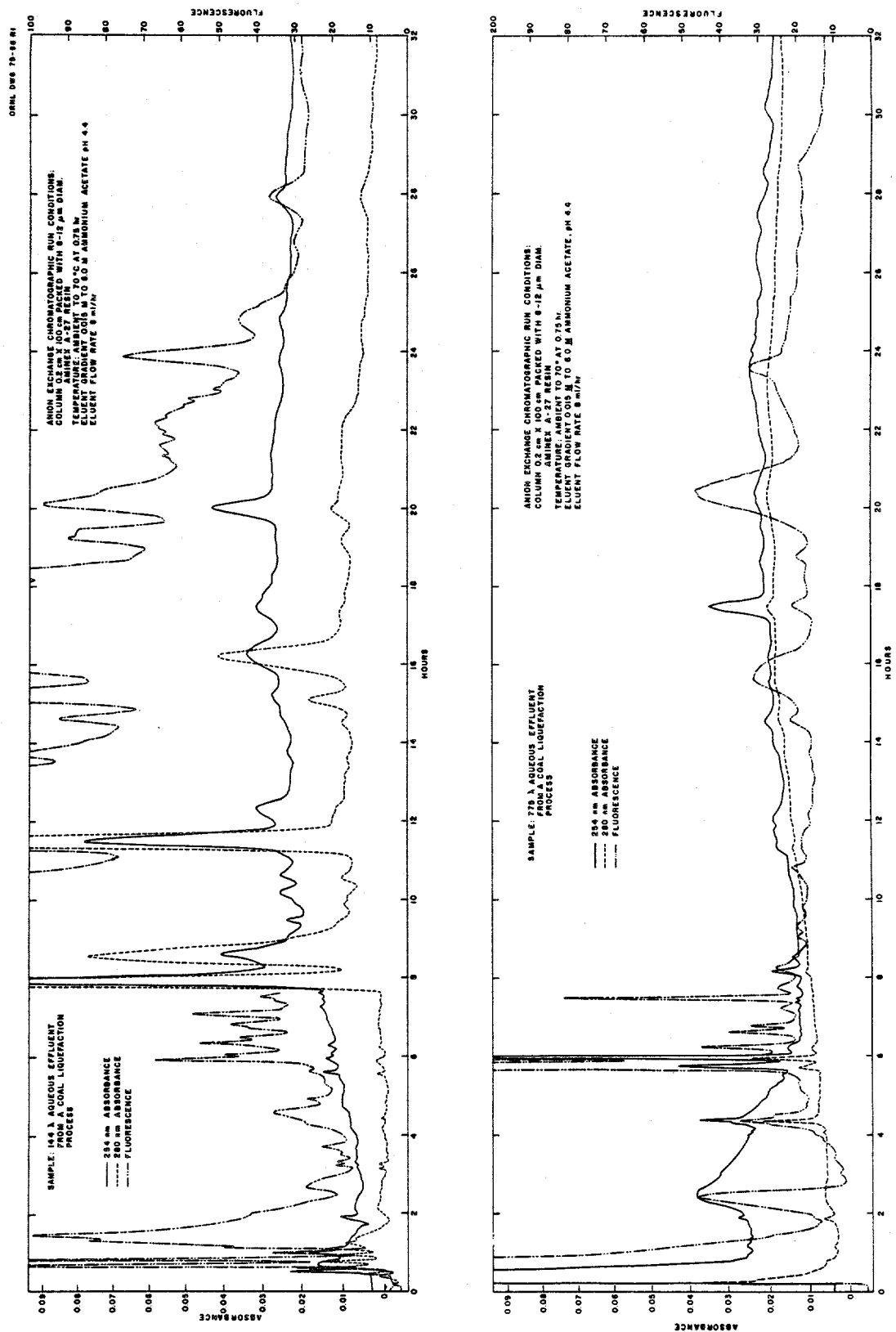


Figure 5.4 Chromatograms of uv absorbing and cerate oxidizable constituents in the product separator (top) and the dryer-stage, first off-gas scrubber (bottom) of a coal-char oil processing plant.

This information concerning phenolic and other compounds in coal-processing waste streams is of great importance with respect to assessing the possible environmental impact of coal-conversion plants. The data on chemical composition of such effluents will also provide feedback information for modification of engineering and plant flowsheets. A liquid chromatograph with a dual wavelength uv photometer and a cerate oxidative monitor was constructed for use in analyzing the efficacy of biological treatment of the phenolic wastes from coal processing plants.

A sample of drinking water from a large midwestern metropolis was examined using HPLC. Only eight major uv-absorbing and/or cerate oxidizable chromatographic peaks were detected and separated during the preparative-scale chromatography of a 4000-fold concentrate of the chlorinated potable water sample. Six unknown organics were characterized and the following four identified and quantified: inositol, 0.5 ppb; o-methylinositol, 11 ppb; mannitol, 0.7 ppb; and succinic acid, 8 ppb. In addition dioctylphthalate, and glycol-1-phthalate were identified by gas chromatography-mass spectrometry in a methylene chloride extract of the water sample.

Organo-phosphorous compounds occur in natural and process waters. The identification of these compounds is of much practical interest because of the eutrophication problem and because phosphates are considered to be a major limiting factor with respect to the formation of biomass. In a cooperative effort with The University of Tennessee, HPLC has proved to be useful for separating organophosphates. A culture of Chlamydomonas reinhardtii, an algae associated with eutrophic waters, was inoculated with  $^{32}\text{P}$  as orthophosphate (10 microcurie/200 ml cul-



ture). Over 60 organophosphorous constituents were separated chromatographically from an unconcentrated filtered water sample of the algal growth.

As part of a cooperative program with other agencies, the effects of chlorination on organics in cooling waters is being investigated using HPLC as a primary separations method.<sup>22</sup> Samples from Watts Bar Lake and the Mississippi River were chlorinated using reaction conditions and chlorine dosages similar to those at the Kingston Steam Plant on Watts Bar Lake and at the Allen Steam Plant on the Mississippi River. The chlorinations yielded 0.5% and 3% chloro-organics from the Watts Bar Lake sample and the Mississippi River sample, respectively. The chromatographic peaks from the two chlorinated cooling water samples were correlated with previous studies of sewage effluents based upon correspondence of elution position and chromatographic patterns. Several peaks were tentatively identified and quantified using previously developed methodology.<sup>23,24</sup> The identifications and values are given in Table 5.3. Two of the compounds have been examined for toxic properties at the part-per-billion level and have been found to significantly lower the hatchability of carp eggs.<sup>25,26</sup> A significantly larger effort should be made to understand the effects of cooling water chlorination and to identify the chlorinated products. It is apparent that even at the low reaction yields determined several hundred tons of chlorinated organics are formed annually during cooling water chlorination and are released to the nation's surface waters.

Since estuarine and marine sites are being used and are under active consideration for both conventional and nuclear electric-power

Table 5.3. Tentative identifications and estimated concentrations of chloro-organic compounds in a typical chlorinated effluent from a municipal sewage treatment plant and chlorinated cooling waters from electric-power producing plants.

Tentative Identification and Chemical Class	Concentration (microgram/liter)		
	Sewage Effluent <sup>a</sup>	Watts Bar Lake <sup>b</sup>	Mississippi River
Nucleoside			
5-chlorouridine	1.7	0.6	7
Purine			
8-chlorocaffeine	1.7	1.1	6
6-chloro-2-aminopurine	0.9	1.0	3
8-chloroxanthine	1.5	3	—
Pyrimidine			
5-chlorouracil <sup>c</sup>	4	0.6	3
Aromatic acid			
2-chlorobenzoic acid	0.3	1.1	10
3-chlorobenzoic acid <sup>d</sup>	0.6	0.2	8
4-chlorobenzoic acid	1.1	0.3	8
3-chloro-4-hydroxybenzoic acid	1.3	0.8	3
4-chloromandelic acid	1.1	1.8	6
4-chlorophenylacetic acid	0.4	3	20
5-chlorosalicylic acid	0.2	3	18
Phenol			
4-chloro-3-methylphenol	1.5	0.2	0.7
2-chlorophenol	1.7	0.2	4
3-chlorophenol <sup>d</sup>	0.5	0.2	
4-chlorophenol	0.7	0.2	2
4-chlororesorcinol <sup>c</sup>	1.2	0.5	7

<sup>a</sup>Reference 24.

<sup>b</sup>Reference 22.

<sup>c</sup>Tested for biotoxicity: References 25 and 26.

<sup>d</sup>Present as a mixture. Concentrations are calculated as if each were the only compound in the chromatographic peak.

generating plants, information concerning the organic constituents in the estuarine waters is necessary for assessing and predicting environmental effects of biocide use for antifoulant purposes. This was graphically illustrated during consultations with Dr. Wallace Davis, III, of Yankee Atomic Electric Company, Westboro, Massachusetts. Estuarine waters are believed to be the "nurseries" of the marine fisheries. Detrimental effects at such sites, because of biocide use, may have far-reaching consequences. Therefore, preliminary investi-

gations were made concerning the concentration and HPLC analysis of an estuarine water sample.

Several concentrations of one-liter aliquots from a 40-liter grab sample of the Cooper River estuarine waters at Charleston, S. C., were made in an effort to overcome the problems created by copious precipitation of inorganic salts and consequent co-precipitation of occluded organics. Although not fully optimized, concentration by desalting with a weak cation exchanger followed by vacuum distillation provided concentrates satisfactory for chromatography. Fourteen uv-absorbing and/or cerate oxidizable peaks were separated during the high-resolution liquid chromatographic analysis of this sample.

In summary, we have developed HPLC as a very useful technique for the separation and detection of trace levels of organic compounds of many types in natural and polluted waters, and we have applied our techniques to several important studies.

## 5.6 References

1. C. J. Sparks, Jr., O. B. Cavin, L. A. Harris and J. C. Ogle, Trace Substances in Environmental Health-VII. D. D. Hemphill (Ed.). University of Missouri, Columbia. pp. 295-304 (1974).
2. C. J. Sparks, Jr., "Quantitative X-Ray Fluorescent Analysis Using Fundamental Parameters." To appear in Advances in X-Ray Analysis, Vol. 19. R. W. Gould et al. (Ed.). Plenum Press, N. Y. (1975).
3. C. J. Sparks, Jr. and J. C. Ogle, Proceedings of First Annual NSF Trace Contaminants Conference. Oak Ridge National Laboratory, Oak Ridge, Tenn. pp. 8-10, CONF-730802. pp. 422-438 (August, 1973).
4. F. Claisse, "Accurate X-Ray Fluorescence Analysis Without Internal Standard." Norelco Reporter, 3, p. 3 (1957).
5. M. L. Perlman, E. M. Rowe and R. E. Watson, "Synchrotron Radiation-Light Fantastic." Physics Today, 30-37 (July 1974).
6. W. Fulkerson, W. D. Shults, and R. I. Van Hook, Ecology and Analysis of Trace Contaminants Progress Report, October 1973 - September 1974. ORNL-NSF-EATC-11. pp. 112-119 (1974).
7. R. W. Stelzner, H. S. McKown, J. R. Sites, Computerized Spark-Source Mass Spectrometer Densitometry. Presented at the American Chemical Society Spring Meeting. Philadelphia, Pa. April 6-11, 1975.
8. J. A. Carter et al., "Mass Spectrometry Development." Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1974. ORNL 5006. pp. 46-48.
9. J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, "Multi-Element Isotope Dilution Spark-Source Mass Spectrometry." Presented at 23rd Ann. Conf. on Mass Spectrometry and Allied Topics, Houston, Texas. May 11-16, 1975.
10. J. A. Carter, D. L. Donohue, J. C. Franklin and R. W. Stelzner, "Environmental and Fuel Materials Analyses by Multi-Element Isotope Dilution Spark-Source Mass Spectrometry." Presented at the 9th Ann. Conf. on Trace Substances in Environmental Health, University of Missouri, Columbia, Mo. June 10-12, 1975.
11. J. A. Carter et al., "Organic Mass Spectrometry." Anal. Chem. Div. Annu. Progr. Rep. Sept. 30, 1974. ORNL 5006. p. 50.
12. C. A. Andersen and J. R. Hinthorne, "Thermodynamic Approach to the Quantitative Interpolation of Sputtered Ion Mass Spectra." Anal. Chem. 45, 1421 (1973).
13. David Simons, University of Ill. Private communication. To be published.

14. R. E. Honig, Advances in Mass Spectrometry, Vol. III. W. L. Mead (Ed.). The Institute of Petroleum, London, Eng. p. 101 (1966).
15. W. L. Harrington, R. K. Skogerboe, and G. H. Morrison, Anal. Chem. 35, 1480 (1965).
16. J. A. Carter, A. E. Cameron and J. A. Dean, "Spark-Source Mass Spectrographic Techniques for the Analysis of Lanthanide and Actinide Elements in Microgram and Sub-Microgram Transuranium Samples." Anal. Lett. 4, 351-55 (1971).
17. Y. Talmi and V. E. Norvell, "A Rapid Method for the Determination of  $\text{CH}_3\text{HgCl}$  at the Part Per Trillion Level in Water Samples Using the Gas Chromatograph-Microwave Emission Spectrometric Detector System." Submitted to Anal. Chem. (Sept. 1975).
18. Y. Talmi and D. A. Bostick, "Determination of Alkylarsenic Acids in Pesticide and Environmental Samples by Gas Chromatography with a Microwave Emission Detector System." Anal. Chem. In press. (1975).
19. Y. Talmi and D. A. Bostick, "The Determination of Arsenic and Arsenicals." J. Chromat. Sci., 13, 231 (1975).
20. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report October 1973 - September 1974. ORNL-NSF-EATC-11. p. 128 (December 1974).
21. R. L. Jolley, S. Katz, J. E. Mrochek, W. W. Pitt, Jr., and W. T. Rainey, "Analyzing Organics in Dilute Aqueous Solutions." Chem. Tech., 312 (1975).
22. R. L. Jolley, C. W. Gehrs, and W. W. Pitt, Jr., "Chlorination of Cooling Water: A Source of Chlorine-Containing Organic Compounds with Possible Environmental Significance." In Proceedings of the Fourth National Symposium on Radioecology, Corvallis, Oregon. In press (May 12-14, 1975).
23. R. L. Jolley, "Determination of Chlorine-Containing Organics in Chlorinated Sewage Effluents by Coupled  $^{36}\text{Cl}$  Tracer--High-Resolution Chromatography." Environ. Letters 7(4), 321 (1974).
24. R. L. Jolley, "Chlorine-Containing Organic Constituents in Chlorinated Effluents." J. Water Pollut. Contr. Fed. 47(3), 601 (1975).
25. C. W. Gehrs, L. D. Eyman, R. L. Jolley, and J. E. Thompson, "Effects of Stable Chlorine-Containing Organics on Aquatic Environments." Nature 249(5458), 675 (1974).

26. C. W. Gehrs and R. L. Jolley, "Chlorine Containing Stable Organics: New Compounds of Environmental Concern." In Proceedings of the International Association of Limnology, Winnipeg, Manitoba. In press (August 22-29, 1974).

## 6. AQUEOUS ABATEMENT TECHNOLOGY

### 6.1 Introduction

The work described in this section concerns the development of two methods for recovering trace quantities of toxic materials from aqueous discharges or process streams. These methods are solvent extraction using high molecular weight amines and electrolytic reduction using high surface area porous or packed bed electrolytic cells.

Although solvent extraction has a rich history as a unit process in the nuclear and petroleum industries, there has been little effort to apply it to pollution abatement. The phenomenal affinity of certain high molecular weight amines for anionic species such as cyanide or metal cyanide complexes coupled with the hydrophobic nature of these amines has led us to investigate their use for abatement applications. On the other hand, the usefulness of electrochemical techniques has already been demonstrated for abatement problems. The full potential of this method depends on improved cell design, which is where our efforts are currently directed.

Unfortunately, there is no universal waste treatment technique which will be suitable for all aqueous wastes, and this also holds true for solvent extraction and electrochemical recovery. Generally each type of waste must be treated as a unique problem. We have therefore experimented with actual waste materials supplied by cooperating industries. Our objective has been to bring the techniques to a state of development at which the applicability and feasibility

are demonstrated and the cost estimated. At that point it will be up to industry to take over further development.

6.2 Removal and Recovery of Pollutants from Industrial Effluent  
Solutions by Solvent Extraction W. E. Bayless, W. S. Groenier,  
and F. L. Moore<sup>a</sup>

One of the more promising emerging technologies for industrial pollution abatement is the solvent extraction approach. In previous reports<sup>1-5</sup> we described the development of new solvent extraction processes for the removal and recovery of mercury and cadmium from industrial chloride solutions. Preliminary results were also presented on the removal and recovery of zinc, cadmium, and cyanide from electroplating waste solutions. Further chemical studies of zinc<sup>6</sup> and cadmium<sup>7</sup> cyanides are described in the open literature. During this reporting period we focused on the removal and recovery of cyanide and zinc from actual effluents of an industrial electroplater. Considerable emphasis was directed to the evaluation of various flowsheets in our miniplant.

Our major objectives are (1) to "close the loop" by recovering and recycling costly chemicals (cyanide, metals) now wasted, (2) to eliminate current troublesome and expensive sludge problems, and (3) to recycle the decontaminated water for reuse in the plant, thereby minimizing sewer taxes and raw water costs - the major operating expenses of many plants. Of major importance is the fact that the

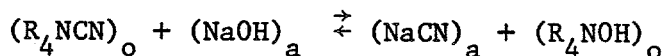
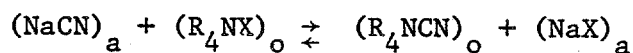
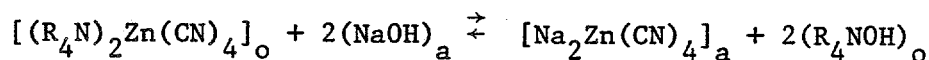
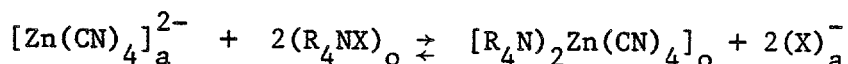
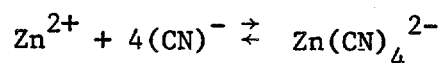
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<sup>a</sup>Task Leader.



treated water may be recycled, thus eliminating a large fraction of the total effluent volume. The Environmental Protection Agency is encouraging reductions in water discharge volumes in addition to lowering pollutant concentrations in the effluent streams.

6.2.1. Chemical Studies. The chemical basis of the process under development is summarized in the following equations:



where  $\text{R}_4\text{NX}$  is selected quaternary amine chloride, hydroxide, or nitrate, "a" signifies the aqueous phase and "o" the organic phase. The quaternary amine and its salt with the anionic cyano complex of zinc are essentially insoluble in aqueous solutions but highly soluble in most organic solvents. Excess cyanide ion is also extracted from the aqueous phase into the organic solvent. The loaded solvent may be regenerated by stripping the cyanide and zinc cyanide with dilute sodium hydroxide.

Numerous diluents for the amine may be used in laboratory work. Amsco 125-82 is probably the most attractive process diluent, because

it is relatively inert, inexpensive, and known to be a satisfactory solvent for process applications. A solvent modifier is required with the aliphatic Amsco diluent to increase amine salt solubility and improve the mechanical phase separation. We found tridecyl alcohol (TDA) to be a satisfactory modifier.

Prior to miniplant evaluations, we performed equal-volume single-stage batch extractions and strippings of cyanide and zinc using an actual industrial rinse solution. The waste solution contained 40.6 ppm cyanide, 23.2 ppm zinc, 0.01 M sodium hydroxide, small amounts of sodium carbonate, and proprietary additives of unknown composition. Zinc extractions from 0.01 M NaOH rinse solution are very efficient (Table 6.1) and useful extraction coefficients are obtained for process applications up to about 0.15 M NaOH. Higher concentrations of amine are required for efficient extraction from more alkaline solutions. Volume concentration factors for zinc were as high as 100 for extraction (Table 6.2) and an additional 10 for stripping (Table 6.3) with dilute sodium hydroxide in a single stage. The most attractive strippant for cyanide and zinc found to date is sodium hydroxide,

Table 6.1. Extraction of Zinc from  
an Electroplating Waste Solution  
with 0.1 M Adogen 464-Cl-Amsco  
(5% TDA)

Aqueous Phase NaOH, M	Percent of Zinc Extracted
0.006	99.0
0.01	98.0
0.03	92.1
0.05	87.1
0.08	80.0
0.10	75.2
0.15	65.2
0.20	56.2

Table 6.2. Concentration of Zinc by Solvent  
Extraction with 0.1 M Adogen 464-Cl-Amsco (5% TDA)

Organic/Aqueous Volume	Organic Concentration Factor	Percent of Zinc Extracted
5/5	1	99.0
5/10	2	99.1
5/50	10	99.3
3/75	25	99.0
4/200	50	99.6
5/500	100	90.6

Table 6.3. Concentration of Zinc by  
Sodium Hydroxide Stripping

Organic/Aqueous Volume	Strippant Concentration Factor	Percent of Zinc Stripped	
		2 M NaOH	6 M NaOH
5/5	1	98.2	99.8
10/5	2	96.7	99.6
50/5	10	83.9	98.9
200/4	50	48.4	72.8

because it offers the possibility for direct recycling of these chemicals back to the electroplating baths. The strippants<sup>4</sup>, sodium hypochlorite and formaldehyde, can also be used but are limited to batch type work, are expensive, and suffer from metal sludge formations - disadvantages we desired to avoid in developing a closed-loop process.

Cyanide ion extracted and stripped essentially quantitatively under the conditions cited above for zinc.

6.2.2 Miniplant Studies. The laboratory-scale mixer-settler miniplant described previously<sup>3-5</sup> was used to evaluate various solvent extraction flowsheets for the removal and recovery of cyanide and zinc from 100 liters of electroplating waste rinse solutions. Operation was similar to that described last year<sup>4</sup>. A schematic flowsheet for

the miniplant operation is shown in Fig. 6.1. The water from the first rinse of the electroplating plant was used as the feed solution for the miniplant. No pH adjustment was required. In the continuous countercurrent solvent extraction process, the amine solvent contacts the aqueous rinse solution to extract zinc and cyanide in two stages. The decontaminated aqueous raffinate solution can either be recycled to the rinse bath in the plating plant or discharged to the sewer. The loaded organic solvent containing the zinc and cyanide is then regenerated in the stripping section by contacting it with dilute NaOH in two stages. The sodium hydroxide concentrate, containing the cyanide and zinc, can be either recycled to the electroplating bath or salvaged. The regenerated solvent is recycled to the extraction section. The process was run at the following flow rates: feed

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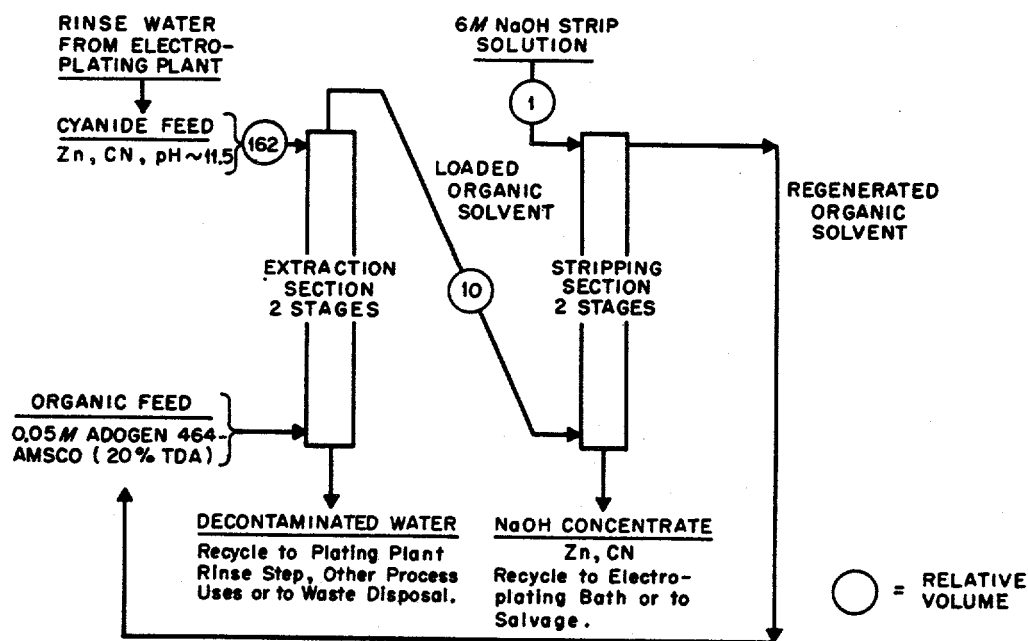


Figure 6.1 Schematic flowsheet for removal and recovery of zinc and cyanide.

solution, 650 ml/min; solvent, 40 ml/min; strippant, 4 ml/min. The overall concentration factor was about 162.

In previous runs<sup>4</sup> using 0.05 M Adogen 464-C1-Amsco (5% TDA), excellent removal and recovery of cyanide and zinc were achieved. However, solubility losses of the amine extractant to the aqueous raffinate were excessive, usually in the 150-300 ppm range. To further reduce the amine losses in the initial extraction steps, we modified the solvent by increasing the tridecyl alcohol concentration. Studies showed that tridecyl alcohol concentrations greater than 5% improved the mechanical phase separations, greatly reduced the aqueous solubility of the amine, and produced clear raffinate solutions. Presumably, through hydrogen bonding with the alcohol, the amine is held in the organic phase. The extractability of cyanide and zinc was not lowered by high concentrations of tridecyl alcohol, even as great as 75%. In further testing 20% tridecyl alcohol was satisfactory as a solvent modifier. Alternate means of reducing amine losses are by multi-stage contacting of the raffinate solution with fresh organic diluent or by treating it with active carbon.

Sixty miniplant runs have been performed to date. Results of a typical run using the process flowsheet (Fig. 6.1) are shown in Table 6.4. The solvent was 0.05 M Adogen 464-Amsco (20% TDA). Extraction and stripping of cyanide and zinc throughout the process were essentially quantitative. Amine losses to the aqueous raffinate averaged in the 30-50 ppm range. In all cases treatment with active carbon readily reduced the amine content of the raffinates to less than 0.1 ppm; moreover, the small amounts of residual cyanide and

Table 6.4. Summary of Typical Miniplant Process Results  
for Removal and Recovery of Cyanide and Zinc

Process Solution	NaOH,M	CN,ppm	Zn,ppm	Adogen 464,ppm	COD <sup>a</sup> ,ppm
Feed solution	0.007	40.6	23.2	—	—
Decontaminated water (raffinate) after sol- vent extraction process	0.006	0.4	0.07	60	209
Decontaminated water after solvent extraction process + active carbon treatment	0.005	<0.2	0.02	<0.1	59
Strippant product	6	2890	1830	<1	—

<sup>a</sup>Chemical oxygen demand

zinc were further reduced to very low levels. The chemical oxygen demand was also reduced substantially by treatment with active carbon.

The technical feasibility of the solvent extraction process was further evaluated by exhaustive testing. A series of eight runs were performed in the miniplant, recycling the regenerated solvent throughout the runs. The process operated well with excellent extraction and stripping of cyanide and zinc and no solids build-up. Interestingly, the amine losses to the raffinate solution decreased regularly in each run, dropping from 70 ppm initially to 8.5 ppm in the eighth run. For many industrial uses of the decontaminated water, it is probable that further treatment with active carbon would not be required.

Chemical reagent costs for the process are very low; a preliminary estimate based on the laboratory-unit demonstrations is less than one dollar per thousand gallons of water treated. This cost is subject to confirmation later in pilot plant tests which are required for realistic estimates of capital and operating costs. The total costs will be compared with the savings which accrue through the recovered

water, metal, and cyanide. Credit from these recovered items in this low-energy process suggests considerable potential savings when one considers the current abatement processes used. The latter methods are destructive in nature and involve the expenses associated with (1) the cost of sodium hypochlorite (or chlorine) and alkalies to destroy cyanide and subsequent water treatment, (2) cost of replenishing the destroyed sodium cyanide and (3) costs of sludge treatment, hauling, and land-fill. Environmental advantages attained through the implementation of a treatment system must also be factored into a cost balance to arrive at cost vs. benefit comparisons. Further environmental benefits beyond the base case of a treatment system may be attained at the additional cost of more solvent extraction and stripping stages.

6.2.3 Current Status, Conclusions and Recommendations. During the 3 1/2 years duration of this project, our studies have shown that the solvent extraction approach is a most promising one for pollution abatement of selected industrial waste solutions. Our initial chemical investigations led to the development of several new practical process flowsheets. We designed and fabricated a flexible laboratory-scale miniplant which was used for the successful demonstration of processes for the removal and recovery of (1) cyanide and zinc from electroplating wastes and (2) mercury from industrial brine solutions. Among other accomplishments during the project are nine technical papers, one patent issued, and two more patent applications. Over 600 inquiries, primarily from industry, have been received in regard to our studies.

The work has also spawned several "spinoffs" now being applied by other chemists.

For future work we recommend:

1. Additional miniplant work is needed on the zinc cyanide process to provide the process engineer with more data for pilot plant design, e.g., optimization of flow rates, stage numbers, and selection of the most practical polishing filter to remove the last traces of amine from the raffinate solution where required.
2. Waste cadmium cyanide rinse solutions should be processed in the miniplant. Chemical studies have been essentially completed for cadmium cyanide but the process has not been demonstrated yet.
3. Other cyanide waste streams containing Au, Ag, Ni, and other valuable metals should be evaluated in the process. In addition to eliminating pollution problems, recovery of these values promises to materially offset the operating cost of the process.
4. Because the solvent extraction process is so highly efficient for the removal and recovery of cyanide, high priority should be given to testing waste effluents from the steel, iron, chemical, and related industries.
5. With the growing concern about organic pollutants in the environment, the solvent extraction process should be evaluated for pollution abatement applications in this area. For instance, the process developed here is capable of removing phenols, organic acids, pesticides, and herbicides from waste solutions. The need for better methods of treating brines contaminated with acetic acid is discussed in a recent EPA publication<sup>8</sup>. Because our previous experience<sup>9</sup>



indicates that acetic acid is efficiently extracted by selected amines, work should be performed on this promising application.

### 6.3 Electrochemical Recovery of Reducible Inorganic Pollutants from Aqueous Streams A. A. Palko and F. A. Posey<sup>a</sup>

6.3.1 Introduction. This research is concerned with development of efficient porous and packed-bed electrolytic cells for removal and recovery of reducible heavy metal ions from flowing streams. Many industrial effluents contain quantities of reducible heavy metals (lead, mercury, cadmium, silver, etc.) which exceed desirable concentration limits for discharge but which are difficult to treat by conventional chemical methods. Electrolytic cells based upon use of porous or packed-bed electrodes have large ratios of reactive surface area to solution volume, and may be designed to allow efficient removal of dissolved reducible metals even when present at low concentrations<sup>10</sup>. Our studies on porous and packed-bed electrodes have led to design, construction, and testing of two types of laboratory prototype metal-recovery units. One of these may be used for continuous recovery of mercury from chlorine plant process streams or other effluents without the use of foreign reagents and without formation of mercury-bearing precipitates. The other test unit is a versatile, modular metal-removal cell which may be used as part of a closed-cycle metal-recovery system.

In previous progress reports<sup>11-13</sup> we discussed experiments on removal of mercury from chlor-alkali plant brines by porous carbon cathodes along with the effects of solution composition, pH, tempera-

ture, etc., on mercury reduction from aqueous solutions onto carbon substrates. Later studies were concerned with removal of dissolved lead from two different effluents, one obtained from a lead-lead dioxide plating plant<sup>14</sup> and the other from a major manufacturer of organolead antiknock compounds<sup>15</sup>. A comprehensive series of measurements was also carried out on the reduction behavior of lead, copper, cadmium, and some other reducible metals as a function of the medium. In addition, theoretical relations were derived which could be used for estimating the performance of practical-sized metal-recovery cells.

Further work on recovery of dissolved lead from organolead manufacturing plant effluent was carried out using cathodes of lead shot, and a number of alternative metal-recovery cell configurations were tested on both simulated and real plant effluents. The lead-shot cathode did not perform to our satisfaction, and later studies used much more efficient porous carbon cathode structures.

During this report period we have investigated the feasibility of removing dissolved silver from photographic processing solutions<sup>16</sup> onto porous carbon cathodes. In addition, a novel concept for recovery of dissolved mercury from brines was tested. The mercury-recovery cell was designed to function in a continuous manner, allowing periodic removal of liquid mercury from the cell for recycle. Finally, as noted above, these studies have led to development of a very versatile, modular metal-removal cell and, later, to development of an integrated metal-recovery system which comprises the metal-removal cell, a rinse cabinet, and an electroplating metal-recovery cell. The recovery

system is designed to treat 1,000 to 10,000 gpd of effluents or process streams of various types, depending upon solution conductivity and metals content, with recovery of metal removed from the stream in the form of a solid sheet, which could be recycled to plant processes, if desired. Details of these developments are described below.

### 6.3.2 Recovery of silver from photographic fix-wash solutions.

In cooperation with personnel from Eastman Kodak Co., we investigated the feasibility of removing dissolved silver from simulated Kodachrome fix-wash solutions onto porous carbon cathodes. Results of some experimental measurements are shown in Fig. 6.2. A small test cell was used which allowed downflow of solution through a cylindrical porous carbon cathode (diameter = 10 cm; cross-sectional area = 78.5

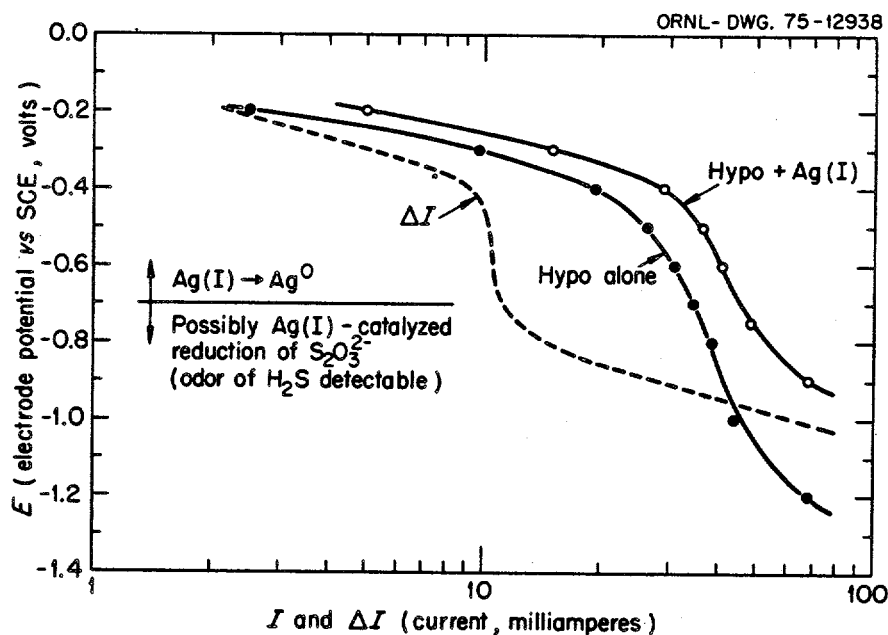


Figure 6.2 Polarization of porous carbon cathode (70 micron average pore diameter) in simulated Kodachrome fix-wash  $1.2 \times 10^{-2} \text{ M S}_2\text{O}_3^{2-} + 5.1 \times 10^{-3} \text{ M SO}_3^{2-} + 2.9 \times 10^{-3} \text{ M Fe (CN)}_6^{4-} + 2.7 \times 10^{-4} \text{ M Ag}^+$  ( $\sim 29 \text{ ppm}$ ). Cathode area:  $78.5 \text{ cm}^2$ ; cathode depth:  $2.54 \text{ cm}$ ; flow rate:  $\sim 1,600 \text{ ml/hr}$ .

$\text{cm}^2$ ; depth = 2.54 cm; average pore diameter = 70 microns; fractional porosity = 0.48) simultaneously with a small upflow through the counter electrode compartment, thus preventing mixing of anode and cathode products. The polarization curves in Fig. 6.2 were obtained at a flow of  $\sim 1,600$  ml/hr with an initial silver content of  $\sim 29$  ppm, and also a "background" curve was run with no silver present. In the absence of silver there was a significant rate of reduction of the hypo solution; the odor of  $\text{H}_2\text{S}$  was detected at the lower potentials. In the presence of silver the polarization curve was shifted and the difference between the curves obtained with and without silver present is shown in Fig. 6.2 as  $\Delta I$ . The curve  $\Delta I$  is due to reduction of silver itself and also to any catalysis of other reduction reactions by the silver ion. At potentials more negative than approximately  $-0.7$  V, a typical mass-transport-controlled current plateau is observed; in this potential region all forms of silver (complexed and uncomplexed) are reduced (the current observed at the plateau is given closely by Faraday's law). These results were obtained at a comparatively low flow rate so that essentially all silver was removed during passage of the fluid through the porous cathode. At electrode potentials more positive than about  $-0.7$  V, another reaction occurred, probably reduction of hypo catalyzed by silver ion (perhaps a  $\text{Ag}^+ - \text{S}_2\text{O}_3^{2-}$  complex). The odor of  $\text{H}_2\text{S}$  was detectable in this lower potential region, simultaneously with formation of  $\text{Ag}_2\text{S}$  slimes on the cathode. The results showed that, although silver recovery from dilute hypo solutions onto porous carbon cathodes was feasible, the cathode potential must be

maintained more positive than approximately  $-0.6$  V vs. the saturated calomel electrode (SCE).

A number of experiments were carried out on the effect of solution flow through the porous carbon cathode on removal efficiency. Such data are required for successful extrapolation of test results on small cells to what could be expected for practical-sized cells.

Some experimental results and an extrapolation are shown in Fig. 6.3. Other work<sup>12</sup> has shown that metals removal on porous carbon cathodes follows a relation of the form  $C(\ell) = C_0 \exp [-B(\ell/U)^{2/3}]$ , where  $C_0$  is the metal ion concentration in the incoming stream,  $C(\ell)$  is the concentration after passage through an electrode of depth  $\ell$  (cm),  $U$  is superficial linear flow rate (cm/sec), and  $B$  ( $\text{sec}^{-2/3}$ ) is a constant which

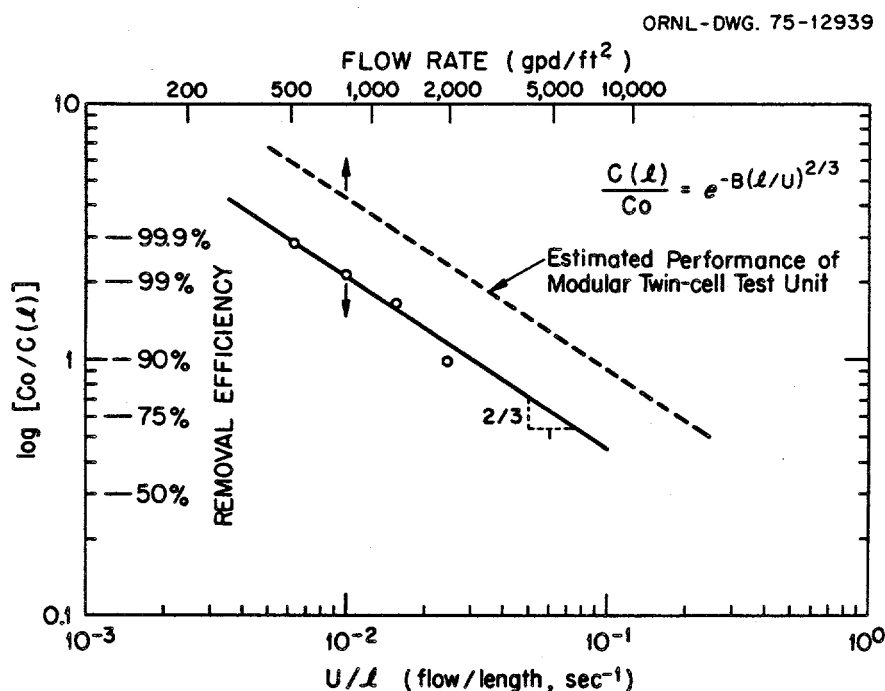


Figure 6.3 Variation of removal efficiency with flow rate for deposition of silver from simulated Kodachrome fix-wash onto porous carbon cathode. Data points obtained with cathode depth of 2.54 cm. Dashed line refers to estimated performance of modular twin-cell test unit.

depends on the characteristics (porosity, average pore diameter, etc.) of the porous electrode. The lower abscissa in Fig. 6.3 is the reciprocal of the average residence time; removal efficiency is indicated on the ordinate. These results were obtained by comparing the silver concentrations of influent and effluent streams which were determined by atomic absorption spectrophotometry. The results were used to estimate the performance of the twin-cell test unit described below. The upper abscissa shows flow rate in gallons/day-ft<sup>2</sup> through the test cell and the dashed line gives the corresponding expected removal efficiency. A removal efficiency of 99% is projected at a flow of  $\sim 2,500$  gpd/ft<sup>2</sup> for once-through operation; this would reduce 30 ppm of Ag to 300 ppb. Likewise, 99.9% removal (reduction to 30 ppb) could be achieved at a flow of  $\sim 1,360$  gpd/ft<sup>2</sup>. These numbers illustrate some of the potentialities for once-through operation of a practical-sized porous-cathode metal-removal cell.

6.3.3 Electrolytic cell for continuous recovery of dissolved mercury. A new electrolytic cell for continuous recovery of dissolved mercury from brines or other aqueous streams was tested which is based upon use of a packed-bed cathode of compressed copper (or other metallic) turnings (or shot, sized particles, chips, etc.). Figure 6.4 is a photograph of the assembled laboratory test cell. The experimental cell was constructed from a 12" length of glass pipe (3" I.D.). Lucite flanges at the ends of the glass pipe incorporated the required fittings and adapters. The cathode structure was a 1"-diameter cylinder of copper screen packed with compressed fine copper turnings.

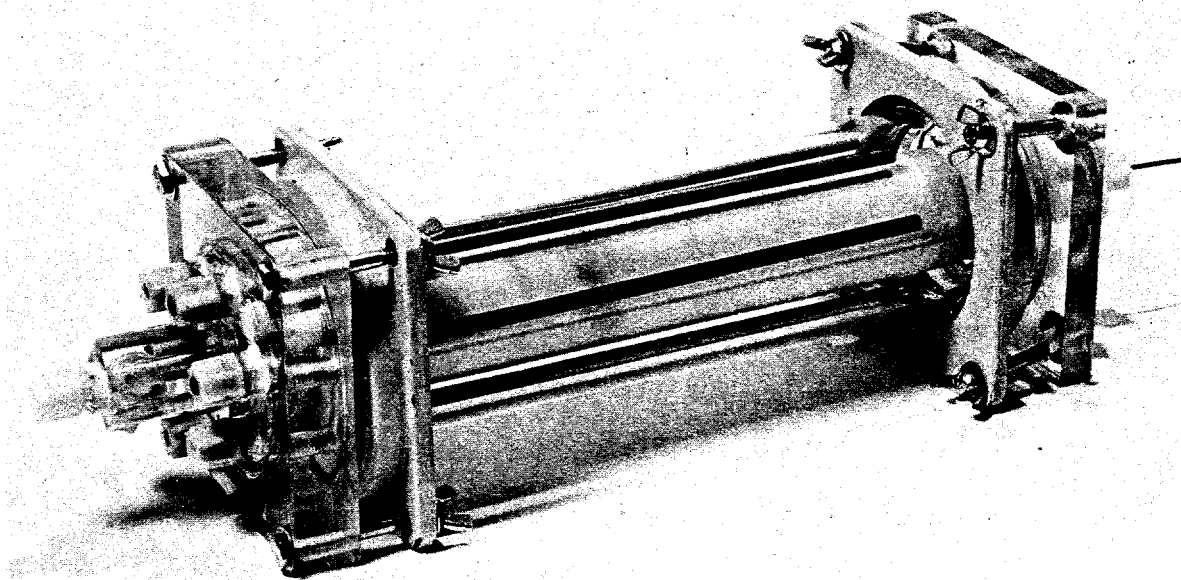


Figure 6.4 Photograph of assembled laboratory cell for continuous recovery of dissolved mercury from streams.

The screen, in turn, was wrapped with a cation-exchange membrane. The experimental cell used du Pont's "Nafion" perfluorosulfonic acid membrane (10 mil thickness), although other membranes could also be used. The cathode structure was centrally located and was attached to the bottom flange at the fluid inlet. The cell operated with upflow of the stream to be treated through the copper column which was maintained at an electrode potential in the range from  $-0.6$  to  $-0.8$  V vs. SCE. Subsequently the stream flowed downwards around the outside of the membrane, being constrained to do so by a surrounding porous polypropylene cylindrical shell which was attached to the top flange. The porous plastic acted as a flow guide while permitting relatively unrestricted passage of current from the anodes to the cathode bed. The porous shell also prevented chlorine, produced at the anodes, from diffusing to the membrane, where it might shorten

useful membrane life. Finally, in the outermost cylindrical chamber, the stream flowed upwards again past a hexagonal array of carbon rod anodes and out of the cell through fittings in the upper flange.

With continued operation of the cell the quantity of electrodeposited mercury eventually becomes sufficient for formation of mercury drops at the base of the cathode column. The cell is designed so that mercury drops may be collected in a sump from which liquid mercury may be withdrawn periodically for recycle. The solutions investigated experimentally were synthetic chlor-alkali plant brines containing 4.3 - 4.6 M NaCl,  $\sim 10^{-3}$  M HCl, and 10-600 ppm Hg. Flow rates were varied between limits which are equivalent to 600-20,000 gpd/ft<sup>2</sup>. The electrode potential of the packed-bed cathode was maintained at -0.8 V vs. SCE. Under these conditions removal efficiencies were better than 99.9% with feed streams containing up to 600 ppm Hg. For example, at a flow rate which is equivalent to approx. 5,000 gpd/ft<sup>2</sup>, removal efficiency was equal to 99.94%. The cell may be operated continuously for long periods without disassembly or maintenance. No precipitation sludges are produced by this method of mercury recovery, no additional reagents are required, and no other ions (especially metal ions) are added to the process stream. The cell design may be scaled up for high-flow applications with various configurations.

6.3.4 Electrolytic system for recovery of dissolved reducible metals. As a result of the work carried out previously in these studies, it was possible during this report period to design an



integrated, closed-cycle electrolytic metal-recovery system. Figure 6.5 is a schematic diagram of the recovery system. The stream to be treated flows through the modular metal-removal cells. Two cells are indicated in Fig. 6.5, although more could be employed in sequence to remove reducible metals to the desired concentration levels. As shown below in the description of the modular metal-removal cell, reducible metals are removed on vertically-arranged porous carbon cathodes which are inserted into the cells from above. Eventually the passages inside the porous carbon cathodes will become plugged with electrodeposited metal, and the electrodes will need to be regenerated with recovery of the metal which was removed from the stream.

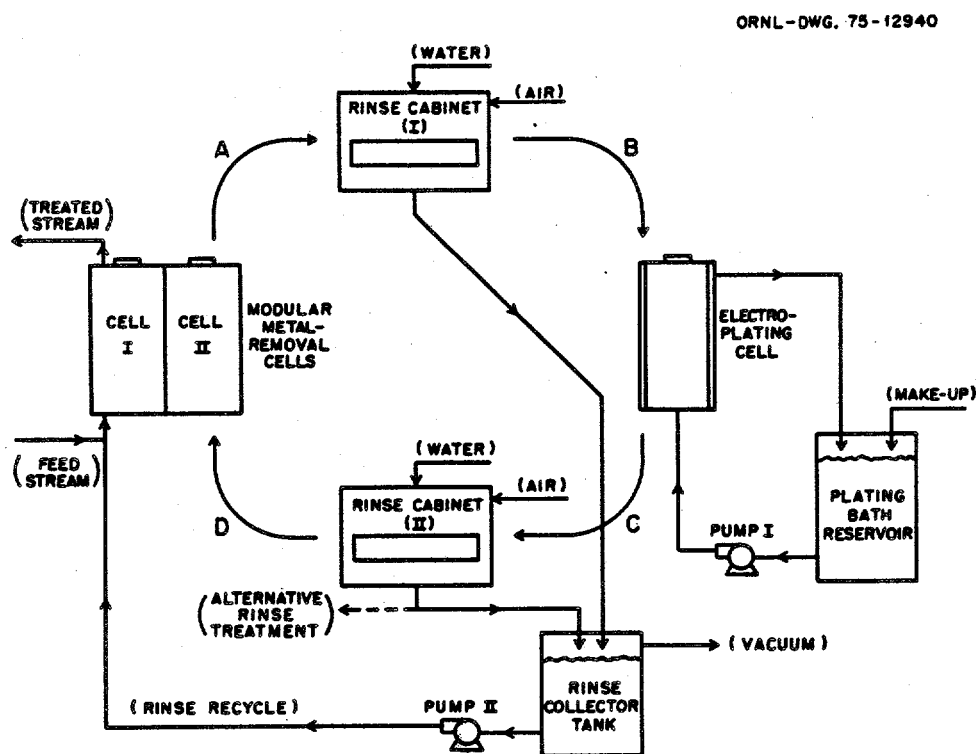


Figure 6.5 Schematic diagram of integrated electrolytic metal-recovery system.

Regeneration and recovery are accomplished by the sequence of steps A through D in Fig. 6.5. In step A electrodes to be regenerated are inserted into rinse cabinet I. Small amounts of water are used to rinse the porous electrode and removal of entrained water is accomplished by manipulation of valves for entry of water and air into the rinse cabinet and of a vacuum valve located at the rinse collector tank. Rinse water from the rinse collector tank may be recycled into the feed stream by pump II. In step B the rinsed and air-blown electrode is transferred to the electroplating metal-recovery cell. Any convenient plating solution may be employed in the loop consisting of the plating bath reservoir, pump I, and the electroplating cell. In this cell the porous carbon electrodes are made anodic while metal is deposited onto sheet or foil "starter" cathodes located on either side of the porous electrode assembly. In favorable cases it should be possible to select the composition of the plating bath so that the solution is compatible with the feed stream and does not add undesirable substances other than reducible metals (e.g., cyanide) to the rinse recycle stream. The stripped porous carbon electrode is transferred in step C to rinse cabinet II. Again the electrode is subjected to water rinsing and air blowing and finally, in step D, the electrode may be transferred back to the metal-removal cell (or placed in standby for eventual use in electrode replacement). Rinse water which cannot be recycled back to the input of the metal-removal cells may be diverted for subsequent treatment by other methods. On the other hand, it may be possible in favorable cases (e.g., recovery of silver from hypo) to make use of a single

rinse cabinet for rinsing electrodes from both the metal-removal and the metal-recovery cells.

A photograph of the modular twin-cell metal-removal test unit is shown in Fig. 6.6 and a cut-away view of a single cell module is shown in Fig. 6.7. The cell body (1) is constructed from Lucite to permit visual observation of cell components. The inlet stream

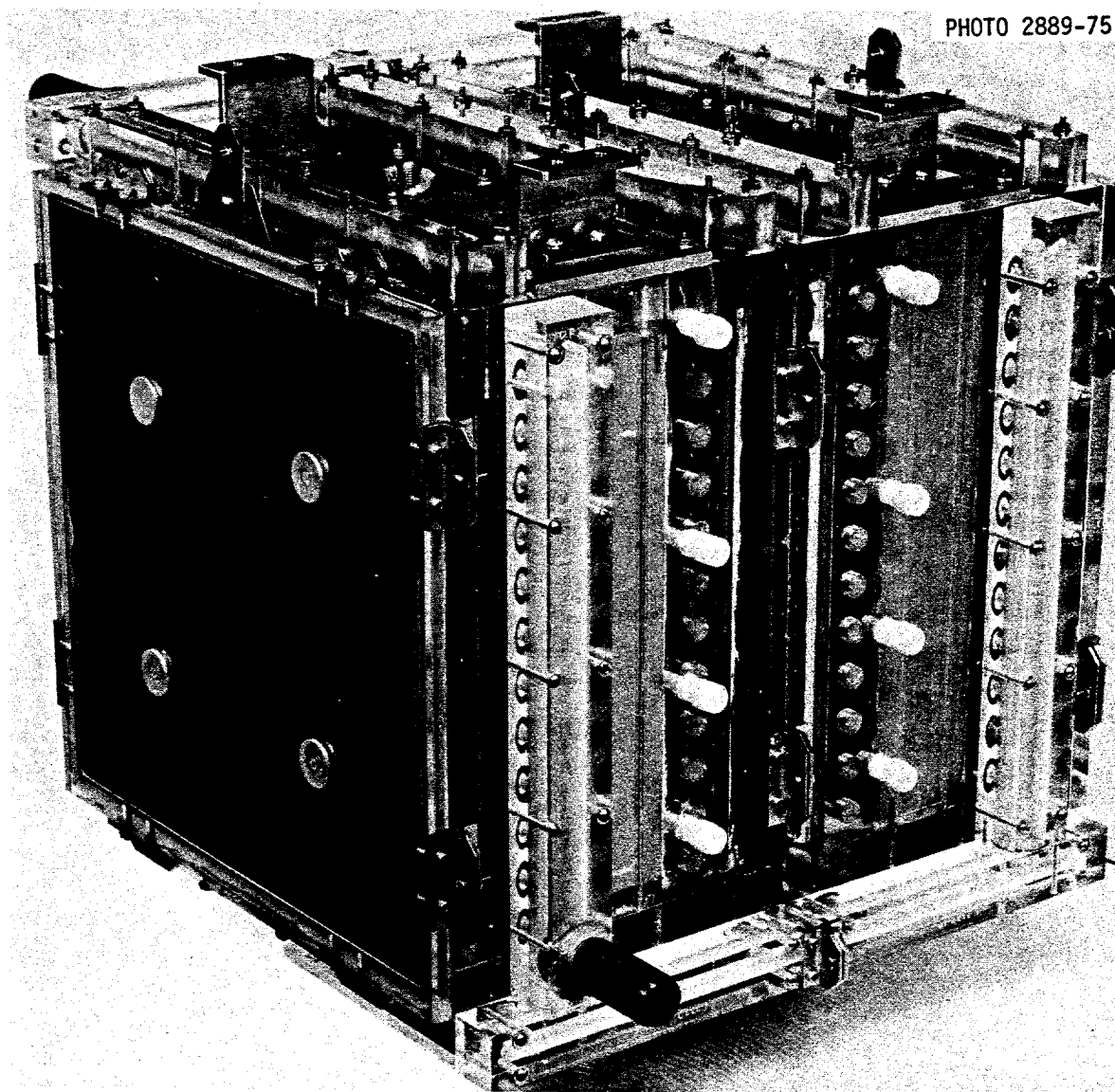


Figure 6.6 Photograph of modular twin-cell test unit for recovery of dissolved reducible metals from flowing streams.

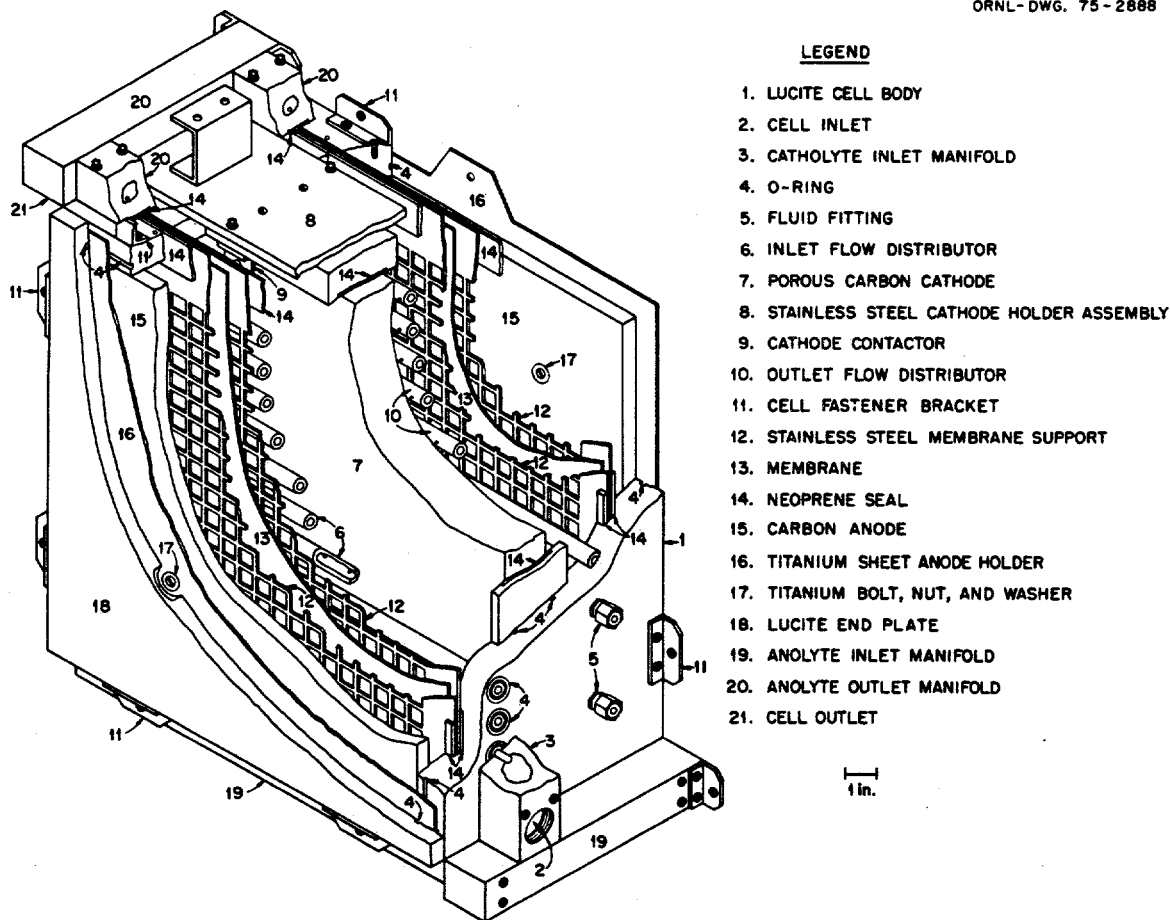


Figure 6.7 Cut-away isometric sketch of metal-removal cell.

enters the cell through a threaded pipe fitting (2) and travels through a catholyte inlet manifold (3), then through a series of inlet flow distributors (6) which is a parallel array of plastic tubes with regularly spaced holes. The stream then flows through the porous carbon cathode assembly, which consists of the porous carbon cathode itself (7) inside a stainless steel cathode holder assembly (8), and various neoprene O-rings (4) and seals (14) so arranged to ensure flow of the stream entirely through the porous cathode. The stream flows horizontally through the cathode and enters another series of flow distributor tubes (10). Subsequently, the stream

flows through an outlet manifold (located at the rear of the cell in Fig. 6.7) and then enters the next modular cell through an inter-cell connector (not shown in Fig. 6.7). After passage through the required number of cells (sufficient for reducing the metal content to the desired level), the stream is recirculated through the anode compartments of the cells. Anode and cathode compartments are separated by use of ionically-conducting membranes (13) which are held in place by perforated membrane supports (12). The membrane supports are sealed at the edges of the cell by neoprene seals to prevent leakage of fluid between cathode and anode compartments. After passage through the porous carbon cathodes in series, the stream enters an array of anolyte inlet manifolds (19) located at the bottom of the cells. Then the stream flows up through holes into channels located between the membrane assemblies and the carbon anode assemblies. The anodes are arranged so that the porous cathode may be polarized from both upstream and downstream sides, thus allowing operation over a much wider range of current demand than in the case of polarization from only one side. The carbon or graphite anodes (15) are bolted to titanium sheets (16) by titanium bolts, washers, and nuts (17). Use of titanium for this purpose is required when the cell is used for treatment of chloride-containing solutions for mitigation of corrosion by chlorine evolved as anode product. After passage of the stream between membrane and anode assemblies, it then flows out holes at the top of the cell into the anolyte outlet manifolds (20) and finally exits from the cell through a threaded pipe fitting (21).

6.3.5 Present status and outlook of work. Construction of the modular metal-removal cell has been completed (cf. Fig. 6.6) and it has been installed in a portable test cabinet with appropriate instrumentation. Upon completion of construction of a test loop, the metal-removal cell will be tested on one or more effluents such as spent photographic processing solutions or organolead plant effluent. Testing of the complete recovery system, including rinse cabinets and the electroplating recovery cell, will be contingent upon continued funding of the work. After testing of the modular metal-removal cell is completed, the results of these studies will be submitted for publication.

#### 6.4 References

1. F. L. Moore, "Solvent Extraction of Mercury from Brine Solutions with High-Molecular-Weight Amines", *Environ. Sci. Technol.*, 6: 625 (1972).
2. W. Fulkerson, W. D. Shults and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report June 1972 - January 1973, ORNL-NSF-EATC-1, p. 349 (March 1973).
3. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report January 1973 - September 1973, ORNL-NSF-EATC-6, p. 333 (January 1974).
4. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report October 1973 - September 1974, ORNL-NSF-EATC-11, p. 140 (December 1974).
5. W. S. Groenier, The Application of Modern Solvent Extraction Techniques to the Removal of Trace Quantities of Toxic Substances from Industrial Effluents, ORNL-TM-4209 (July 1973).
6. F. L. Moore, "Liquid-Liquid Extraction of Zinc with High-Molecular-Weight Amines from Alkaline Cyanide Solutions", *Separ. Sci.*, 10: 489 (1975).
7. F. L. Moore, "Solvent Extraction of Cadmium from Alkaline Cyanide Solutions with Quaternary Amines", *Environ. Lett.*, 10: 1 (1975).
8. R. D. Fox, R. T. Keller and C. J. Pinamont, Recondition and Reuse of Organically Contaminated Waste Sodium Chloride Brines, EPA-R2-73-200 (May 1973).
9. F. L. Moore, "Liquid-Liquid Extraction with High-Molecular-Weight Amines", *National Acad. Sci. Nuclear Science Series NAS-NS-3101* (1960).
10. R. W. Houghton and A. T. Kuhn, "Mass-transport Problems and some Design Concepts of Electrochemical Reactors", *J. Appl. Electrochem.*, 4(3): 173-190 (1974).
11. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report June 1972 - January 1973, ORNL-NSF-EATC-1, p. 367 (March 1973).
12. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report January 1973 - September 1973, ORNL-NSF-EATC-6, p. 360 (January 1974).

13. W. Fulkerson, W. D. Shults, and R. I. Van Hook (Eds.), Ecology and Analysis of Trace Contaminants Progress Report October 1973 - September 1974, ORNL-NSF-EATC-11, p. 146 (December 1974).
14. Union Carbide Corporation, Consumer Products Division, Bennington, Vermont.
15. Ethyl Corporation, Baton Rouge, Louisiana.
16. Eastman Kodak Company, Rochester, New York.



## 7. INFORMATION FLOW AND MANAGEMENT

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### 7.1 Introduction

The Toxic Materials Information Center (TMIC), Information Center Complex, of Oak Ridge National Laboratory provides a variety of information support services to the Trace Contaminants Program of NSF-RANN. The services include (1) creating data bases and answering inquiries on trace contaminants; (2) preparing and publishing bibliographies; (3) establishing a pilot project on tabular environmental data; (4) preparing, publishing and disseminating to approximately 1,000 selected recipients a periodic abstract journal and newsletter covering all research results published by grantees of the nationwide Trace Contaminants Program; (5) maintaining and publishing annually a directory of all personnel participating in the overall Trace Contaminants Program; (6) maintaining a substantial directory of persons engaged in or interested in trace contaminants research throughout the United States and several foreign countries and providing upon request either computerized listings or mailing labels from this directory; (7) selected dissemination of information (SDI) on specific subjects on a monthly basis; and (8) other information support activities including data and document acquisition for the Ecology and Analysis of Trace Contaminants Program members.

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<sup>a</sup>Task Leader

## 7.2 Program-Wide Information Support Activities

Timely and effective communication of research results is an important aspect of Research Applied to National Needs. The use of a specialized abstract journal as a communication and technology transfer tool is particularly applicable in research areas such as trace contaminants because the research cuts across traditional disciplinary boundaries. Thus key results may be published in a wide variety of journals and via governmental report channels, geared for immediate application to broad environmental problems, but not necessarily accessible to the interested wide audience which includes research investigators, applied scientists and engineers, scientific administrators and public decision-makers. The NSF-RANN Trace Contaminants Abstracts<sup>1</sup> (TCA) began publication in 1973 with an initial distribution of 500 copies to persons engaged in or interested in trace contaminants research. Since that time the distribution has grown to approximately 1,000 individuals and/or institutions. Volumes 1 and 2 each comprised four issues; the first issue of Volume 3 is in press. Over 500 publications and presentations from more than 300 researchers in 43 NSF-RANN research grant programs have been abstracted in Trace Contaminants Abstracts. Information of more transient interest to the trace contaminants user community has been disseminated through the newsletter sections of each Trace Contaminants Abstracts issue; this section includes notices of grant approvals, general program announcements, meeting calendar and reviews, personnel news and changes, etc.

As an additional aid to effective communication throughout the NSF-RANN Trace Contaminants Program, the TMIC has maintained since 1973 a directory of participants in all research grants of the Program--by name, address, telephone number, and a very brief description of research interest. The directory is updated and published annually and distributed to the approximately 1,000 recipients of Trace Contaminants Abstracts and others selected by the Trace Contaminants Program managers. When the initial supply is exhausted, copies can be obtained through the National Technical Information Service. The 1975 Directory<sup>2</sup> (in press) contains listings for 325 individuals from 38 active research grants and the program's central office.

The computerization of this directory, the Trace Contaminants Abstracts distribution, and distribution lists of others interested in trace contaminants research allows TMIC to offer additional services in the preparation of special mailing lists and mailing labels upon demand. Special mailings can be categorized by disciplines represented in trace contaminants research such as modeling, analytical measurements, ecological research, abatement, and others. These special directories are part of an overall energy and environment oriented directory data bank of information centers, research projects, and individual investigators established by the Information Center Complex to serve research administrators, scientists, group leaders, and information specialists who need to contact workers active in the energy and/or environmental field.

### 7.3 Information Acquisition and Organization

The information required by EATC research investigators is acquired by TMIC and, when deemed to be pertinent to a larger audience, is organized into one of several types of review documents and/or data bases: (1) literature overview; (2) selected annotated bibliography; (3) extracted data in a tabular format; and (4) resultant computerized data bases. The computerized data bases created by TMIC are summarized in Table 7.1.

A topical literature review on heavy metals and other trace elements in aquatic environments is prepared for the Annual Literature

Table 7.1. Toxic materials information center data bases

Data Base	Entries	Content
TMIC General Data Base	6700	A
Environmental Transport of Chemicals	1200	B,C,D
Transport Through Soil Processes	2000	B,D
Trace Contaminants in Soils and Sediments	1874	B
Environmental Transport Modeling	400	A,C,
Environmental Modeling	600	B
Coal Conversion Processes and Pollutants	2500	
Trace Elements in Coal and Other Fuels	1000	A
Heavy Metals in Aquatic Environments (1973-1974)	744A	A,C,D,F
Trace Elements in Sewage/Sludge	600	A
Trace Substances in Environmental Health Conferences - 7th, 8th, 9th	164	A
Cadmium	4950	A,D
Arsenic	1450	A,D
Mercury	3100	A
Lead	9050	B
Environmental Quality Indicators	600	A,D,E
Resource Center Index	1000	C
NSF-RANN Trace Contaminants Program	407	A,C,D
NSF-RANN Trace Contaminants Program Directory	342	B,D
Trace Contaminants Investigator/Administrator Directory	1000	B

A - file with abstracts

B - file partially with abstracts

C - hard copies available at TMIC

D - published

E - created by W. A. Thomas, G. Goldstein, W. Wilcox ORNL

F - now covered in Resource Center Index

Review issue of the Journal of the Water Pollution Control Federation; this review is a joint project with Dr. H. V. Leland of the United States Geological Survey. The objective of this review is to provide a comprehensive summary of the pertinent annual contribution to the technical literature regarding heavy metals in relation to water pollution. Included within this scope are studies referring to any aquatic ecosystem or any component of an aquatic ecosystem regarding heavy metal occurrence, availability, movement, concentration, activity, effects, toxicity, conversion or removal. The subject of heavy metals in relation to analytical technique or method of determination is incorporated into a separate review for the Water Pollution Control Federation by another author. Over 900 technical papers, reports and theses were considered for incorporation into the two most recent reviews (1974)<sup>3</sup> (1975)<sup>4</sup>. The number of articles being considered for incorporation into the 1976 review is over 700.

A comprehensive data base on environmental transport modeling is being constructed from TMIC's general file on Air, Water, and Environmental Modeling (14,600 citations) and from ORNL's extensive data base and library holdings. The scope of this specialized collection was developed with the assistance of the research team for the Unified Transport Model (Section 3). Documents are being analyzed to eliminate hydrologic models which do not consider solutes, and to eliminate physical simulations. The collection is expected to exceed 1200 annotated citations. When complete, the file will be available for computer searching and will be published in hard copy.

#### 7.4 Information Retrieval and Dissemination

The data bases and information services established by the Toxic Materials Information Center in support of the NSF-RANN Ecology and Analysis of Trace Contaminants Program at ORNL and of the national Trace Contaminants Program have been available in whole or in part to all individuals seeking information regarding this area of research. Such services include in-depth literature searches using computerized data bases and extensive library facilities; the answering of specific environmental questions posed by the scientific community, government agencies, industry, and others; and the publication of bibliographies as natural by-products of the response service. Mechanisms for partial to full cost recovery for such services are being developed in order to allow information resources to be tapped by multiple user groups without financially stressing the government agency funding the original data collection or organization of information.

In addition to the TMIC data bases listed in Table 7.1, Table 7.2 summarizes other computerized data bases available at ORNL for selected dissemination of information (SDI) and retrospective searching.

Some 45 EATC research investigators receive each month computerized searches tailored to individual research interests from these data bases. The major pollution-oriented abstract journals are manually scanned each month for additional citations. A third monthly SDI service is the preparation and distribution of a "current contents"

Table 7.2. Non-toxic materials information center data bases  
available to the information center complex

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Some ICC/ORNL data bases available:

IBP Abstract Journal	Environmental Aspects of the
Ecological Sciences	Transuranics
Regional Modeling	Computer Program Inventory
Energy	Dioxin, Biological Effects of
Environmental Plutonium	Ecological Effects of Strip
Thermal Effects on Aquatic	Mining
Organisms	Environmental Impact of Nuclear
Radionuclide Cycling in Soils	Power Plants
and Plants	World Energy Resources
Ecosystems Analysis	Environmental Law Abstracts
Liquid Wastes	Modeling of Ecological Systems
Chemical Mutagenesis	Environmental Terminology Index
Clinical Toxicology of Commercial	Biogeochemical Ecology
Products	Ecological Succession
Forest Insecticides	Hydrazine, Toxicity of
Modeling Bibliography	Radioecology
Striped Bass	Energy Research and Development
Heated Effluent Bibliography	Inventory

Non-ORNL data bases available:

Nuclear Science Abstracts, Atomic Energy Commission  
 Metals Abstracts, American Society for Metals – metallurgy and related areas of physics and chemistry  
 Chemical Abstracts, Chemical Abstracts Service – Chemistry  
 Chemical-Biological Activities, Chemical Abstracts Service – vivo and in vitro  
 Biological Abstracts Previews and BioResearch Index, BioScience Information Service of Biological Abstracts – life sciences  
 TOXLINE, National Library of Medicine – includes Chemical-Biological Activities, Health Aspects of Pesticides, Toxicity Bibliography, Health Aspects of Environmental Pollutants, Hayes Files, and International Pharmaceutical Abstracts  
 MEDLINE (Medlars on line), National Library of Medicine  
 CHEMLINE, National Library of Medicine – On-Line Chemical Dictionary  
 CANCERLINE, National Library of Medicine – including Carcinogenesis Abstracts and Ongoing Cancer Research  
 CATLINE, National Library of Medicine – Catalog File  
 SERLINE, National Library of Medicine – Biomedical Serials  
 Government research Announcements, National Technical Information Service  
 CAIN, Cataloging and Indexing System, National Agricultural Library – agricultural sciences  
 Name Match System, Chemical Abstracts Service  
 Water Resources Abstracts, Water Resources Information Center of the U.S. Dept. of the Interior  
 ERDA Energy Data Base, Technical Information Center  
 COMPENDEX, Engineering Index, Inc. – includes Bioengineering and Pollution Control  
 DIALOG, Lockheed – including NTIS Reports File, Physics Abstracts Computers and Control Abstracts, COMPENDEX, PANDEX – (Macmillan Information Company's Index to technical literature) TRANSDX (U.S. Joint Publications Research Service Translations), Social Sciences Citation Index, CAIN, and Chemical Abstracts Condensates  
 RECON, Energy Research and Development Administration

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document (selected contents pages from environmental and analytical journals) to the EATC personnel.

#### 7.5 Pilot Project on Environmental Data Extraction

The proliferation of scientific literature in general has given both the research investigator and the information specialist cause to develop more precise information retrieval methods than the traditional ones. Concern for more efficient storage and display of information led to a pilot project on selective extraction, in a tabular format, of environmental data on certain toxic substances. The objective of the Environmental Data Extraction (EDE) pilot project was to determine the feasibility of tabulating scientific and technical data pertaining to the sources, transport, and fate of trace contaminants in the environment.

The six areas of coverage suggested by our advisory committee (W. Fulkerson, W. D. Shults, R. I. Van Hook) were environmental monitoring, transport/persistency, biological uptake/elimination, analytical methodology, environmental standards/criteria, and disposal/abatement. Once these six data areas were adopted, data descriptor fields within each data base were developed and tested for applicability and content definition. The data descriptor fields were refined many times through interaction with EATC user groups and actual extraction experience by TMIC staff members; editing and altering of fields continued until July 1975. Table 7.3 lists the data descriptor fields chosen for the four major data bases. In the application of this data documentation technique to first source references, it was found that the Environmental Monitoring (ENVMONT) Biological Uptake/Elimination (BIOELIM),



Table 7.3. Environmental data extraction data base fields and explanations

Fields of the Data Bases	Environmental Monitoring	Biological Uptake/ Elimination	Analytical Methodology	Disposal/ Abatement
SUB - Substance studied	X	X	X	X
SOURCE - Literature reference	X	X	X	X
MEDIUM - Air, Water, Soil, etc.	X			
ENV SOUR - Environmental source corporation, municipality, etc.	X			X
GEOGRAPH - Geographic location of the study.	X			
DISCHARG - Discharge as form and rate or quantity.	X			
OTHERSUB - Other substances studied.	X			
ORGANISM - Organism studied; common and technical name.	X	X		
COLLECT - Collection methods, sampling techniques.	X			
METHOD - Analytical method.	X	X	X	
RESULTS - Analytical results	X			
COMMENT - Comment on method, results, etc.	X	X	X	X
ROUTENT - Route of entry into organism or medium.		X		
TISSUE - List of tissues that were studied.		X		
CONC/CF - Concentration/Concentration Factor. List value.		X		
BIO H.L. - Biological Half Life		X		
ELIMRATE - Elimination rate, listing of values		X		
DISPOSAL - Disposal/Medium/Quantity				X
ABATPROC - Abatement procedures, techniques				X
MATRIX - Form which sample takes prior to analysis.				
APPLICAT - Applications to different material types.			X	
SENSITIV - Sensitivity of the method used.			X	
ACC/PREC - Accuracy/Precision of the method used.			X	
INTERFER - Interferences by listed elements or compound.			X	
UPRATE - Rate of uptake.		X		

X - Denotes presence of field in the data base.

Analytical Methodology (ANALMETH), and Disposal/Abatement (DISPABT) subject areas were best suited for data extraction. The Transport/Persistency data base did not develop as expected. Though TMIC and the EATC Program continues to build a very comprehensive literature collection in transport, it was not possible to develop consistent patterns in the data due to the lack of uniformity between the several disciplines doing research in this area. The diversity in recording the data pertaining to the transport or persistency of toxic materials in the environment made the concise, accurate recording and storage of data impossible. The Environmental Standards/Criteria data base was not utilized in this year due to the relative lack of data in this area and the previous documentation of data that was available.

The Environmental Monitoring data base was the predominant data base. During the course of information acquisition and input, this area received more than half of all articles computer stored. (See Table 7.4 for sample of data extracted.) The environmental awareness and the subsequent concentration of environmental sampling for toxic materials undoubtedly contributed to the relative size of this data base. The second largest data base was the Biological Uptake/Elimination data base followed by Analytical Methodology and Disposal/Abatement.

These data are stored and retrieved using a computer program written by V. A. Singletary of the Oak Ridge National Laboratory (ORNL) Computer Sciences Division. This program, written in FORTRAN language and called ADTABLE, is part of the ORCHIS system.<sup>5</sup> The data can be

Table 7.4. Environmental monitoring

Substance	Source	Other Substance	Organism	Medium	Environmental Source	Discharge	Geographic Location	Collection	Analytical Methodology	Results	Comments
Copper	Fuge, R. James, K.H. 1974	Zinc, Cadmium	Brown Seaweed FUCUS VESICULOSUS	Water			Nefyn, Caernarvon Bay, Irish Sea	Seasonal	Atomic absorption spectrophotometry	For the month of Sept. 70 analysis of 30 samples gave concentrations of 4.76 plus or minus 0.52 ppm plus or minus S.D.	
Mercury	Clark, D.R. Melane, M.A.R.	MEDIAN	Woodcock (PHILOHELA (MINER)	Insecticides			U.S.A.; Florida	Woodcock were collected from Oct. 1970 through Feb. 1971	Total mercury content determined by cold vapor atomic absorption. Sam- ples digested by refluxing with sulfuric-nitric acid mixture. A mixture of hydroxylamine, stannous chloride, an sulfuric acid was added to the digest to reduce the mercury II ions to mercury metal. Samples were aerated at 3 liters/min. and passed through the absorption cell.	The mercury content median was 0.28 ppm from liver samples and based on wet weight.	
Mercury	Gardner, D. Riley, J.P. 1973			Water			England, Severn Estuary,	Surface sampling in June 1971 and November 1972. Suspended matter removed by con- tinuous centrifuge. Samples temporarily stored in an acidified condition in silicone- coated glass bottles.	Samples analyzed by use of a combined dithizone extraction-flameless atomic absorption tech- nique (Gardner and Riley, 1973)	The dissolved mercury concentration at Lundy Isle on the Bristol Channel was 30 nanograms/liter.	

searched by index terms on practically any field of the particular data base and the information sought can be printed in any format. The computer programs were modified during the year to allow the repetitive information extracted from an article to be represented by a symbol on computer tape that would print the information in its entirety when called upon. The use of symbols lowers tape rental costs, and reduces preparation time of extracted information.

Specific format guidelines for Environmental Data Extraction were developed during the first half of the project year. These guidelines cover punctuation, spelling, subscripts, exponents, superscripts, capitalization, units of measurement, and abbreviation.

Evaluation of the pilot project is not yet complete, but some preliminary conclusions have been drawn in a report being prepared. This report will record the progression of the EDE project, offer some conclusions and suggestions for future applications, and include all the data extracted on mercury, cadmium, and other pollutants (primarily, potential pollutants from coal conversion processes).<sup>6</sup>

## 7.6 References

1. E. D. Copenhaver (editor), NSF-RANN Trace Contaminants Abstracts, Vols. 1, 2, 3; ORNL-EIS-60; Oak Ridge National Laboratory, Oak Ridge, Tennessee (1973-75).
2. B. K. Wilkinson and S. K. Smith, NSF-RANN Trace Contaminants Directory, 1975, Oak Ridge National Laboratory (in press).
3. H. V. Leland, E. D. Copenhaver, and L. S. Corrill, "Heavy Metals and Other Trace Elements", Journal of Water Pollution Control Federation, 46 (6), 1452-1476, (1974).
4. H. V. Leland, E. D. Copenhaver, D. J. Wilkes, "Heavy Metals and Other Trace Elements", Journal of Water Pollution Control Federation, 46 (6), 1635-1656, (1975).
5. A. A. Brooks, Oak Ridge Computerized Hierarchical Information System (ORCHIS) Status Report - July 1973.
6. G. A. Dailey, E. D. Copenhaver, and J. W. Pardue, Environmental Data Extraction: An Experiment in Tabular Data Extraction from Primary Sources (in preparation).



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STUDY:ISOTOPE DILUTION:ION MICROPROBE MASS  
SPECTROMETRY:SPARK SOURCE MASS SPECTROSCOPY

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PROGRAM:MEASUREMENT RESEARCH: DEVELOPMENT AND  
APPLICATION OF MULTI-ELEMENT ISOTOPE DILUTION  
SPARK-SOURCE MASS SPECTROMETRY AND ION MICROPROBE  
TECHNIQUES FOR ENVIRONMENTAL SAMPLES

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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS:TOXIC  
MATERIALS INFORMATION CENTER, TEAM  
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TRACE CONTAMINANTS ABSTRACTS

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CONTAMINANTS:ATMOSPHERIC TRANSPORT MODEL

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS:ECOLOGICAL RESEARCH: ENVIRONMENTAL  
RECONNAISSANCE AND CYCLING. UNIFIED TRANSPORT  
MODEL

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MULTI-ELEMENT IDSSHS AND INMA TECHNIQUES FOR  
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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS:  
MEASUREMENT RESEARCH: SEPARATION, DETECTION AND  
IDENTIFICATION OF ORGANICALLY BOUND TOXIC METALS  
AND OTHER HAZARDOUS MATERIALS: ATOMIC ABSORPTION  
SPECTROSCOPY

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: UNIFIED TRANSPORT  
MODEL: SEDIMENTS: BED LOAD: HEAVY METALS

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: CO-PRINCIPAL INVESTIGATOR: ALLEN  
STEAM PLANT STUDY

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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS:  
MEASUREMENT RESEARCH: ENVIRONMENTAL APPLICATIONS OF  
CENTRIFUGAL PHOTOMETRIC ANALYSIS. TASK LEADER:  
GENSAEC

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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS: GAS  
CHROMATOGRAPHY-MICROWAVE EMISSION SPECTROMETRY

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: ABATEMENT TECHNOLOGY: REMOVAL AND  
RECOVERY OF POLLUTANTS BY SOLVENT  
EXTRACTION

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CHROMATOGRAPHY-MICROWAVE EMISSION SPECTROMETRY

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: ECOLOGICAL RESEARCH: BIOLOGICAL  
TRANSPORT: AQUATIC ECOSYSTEMS

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: UNIFIED TRANSPORT MODEL: ATMOSPHERIC  
TRANSPORT: MODEL: SULFUR

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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS: GAS  
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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS:  
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TRANSPORT: AQUATIC ECOSYSTEMS

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CONTAMINANTS: UNIFIED TRANSPORT MODEL

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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS: ALLEN  
STEAM PLANT STUDY: ESCA: ELECTRON SPECTROSCOPY FOR  
CHEMICAL ANALYSIS

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CONTAMINANTS: ECOLOGICAL RESEARCH: SOILS: PLANT  
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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: MEASUREMENT RESEARCH: MEASUREMENT OF  
THE MOLECULAR ORGANIC CONTAMINANTS IN POLLUTED  
WATER BY LIQUID CHROMATOGRAPHY

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CONTAMINANTS: UNIFIED TRANSPORT MODEL: SOIL  
MOISTURE: TRANSPORT: MODEL: HYDROLOGY

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CONTAMINANTS: ECOLOGICAL RESEARCH: ATMOSPHERIC  
DEPOSITION

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STEAM PLANT STUDY: NEUTRON ACTIVATION ANALYSIS

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: ABATEMENT TECHNOLOGY: REMOVAL AND  
RECOVERY OF POLLUTANTS BY SOLVENT EXTRACTION: TASK  
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CONTAMINANTS: UNIFIED TRANSPORT MODEL

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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS: AIR  
TRANSPORT MODEL: ATMOSPHERIC: CLIMATOLOGY: POLLUTANT  
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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS:  
ABATEMENT TECHNOLOGY: ELECTROCHEMICAL RECOVERY  
OF REDUCIBLE INORGANIC POLLUTANTS FROM AQUEOUS  
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CONTAMINANTS: UNIFIED TRANSPORT MODEL: TEAM LEADER

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CONTAMINANTS: MEASUREMENT RESEARCH: MEASUREMENT  
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OF REDUCIBLE INORGANIC POLLUTANTS FROM AQUEOUS  
STREAMS, TASK LEADER

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS: UNIFIED TRANSPORT MODEL: HYDROLOGIC  
TRANSPORT: ATMOSPHERIC TRANSPORT: SULFUR  
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GASES, TASK LEADER

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ECOLOGY AND ANALYSIS OF TRACE  
CONTAMINANTS:EVALUATION OF ION MICROPROBE FOR  
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ECOLOGY AND ANALYSIS OF TRACE CONTAMINANTS:  
MEASUREMENT RESEARCH: DEVELOPMENT OF HIGH  
SENSITIVITY X-RAY FLUORESCENCE FOR ANALYSIS OF  
TRACE TOXIC ELEMENTS, TASK LEADER: ALLEN STEAM  
PLANT STUDY

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**LIST OF EATC PUBLICATIONS AND ORAL PRESENTATIONS**



**SULCAL: A Model of Sulfur Chemistry in a Plume**  
 Baas, C.F., Jr.; Holdeman, J.T.; Culkowski, W.H.  
 PHONE NO: 615-483-8611, ext. 3-6262

**ORNL-NSF-EATC-21 (In Preparation)**

**SULFUR; ATMOSPHERE; MODELS; MODELING; SULFUR DIOXIDE**

**Documentation and Application of SCREEN: A Model for Soil Chemical Exchange of Heavy Metals**

Begovich, C.L.; Jackson, D.R.

PHONE NO: 615-483-8611, Ext. 3-1615

**ORNL-NSF-EATC-16, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, 67 p.; 1975, Nov.**

**SOIL CHEMISTRY; TRANSPORT MODELS; METALS; TRANSPORT; PARTICULATES; SOIL SOLUTION; CHEMICAL EXCHANGE**

**Hydrologic Transport Modeling**

Batson, R.P.; Huff, D.D.

PHONE NO: 615-483-8611, Ext. 3-6650

**Proceedings of the Conference on Computer Support of Environmental Science and Analysis, ERDA, Held at Albuquerque, NM, July 1975**

**HYDROLOGY; TRANSPORT; MODELS; WATER QUALITY; SIMULATION; DATA NEEDS; TRANSPORT MODELS**

**The Chemical and Biological Behavior of Lead and Cadmium in Shelter-Contaminated Forest Soil**

Bondietti, E.A.; Jackson, D.R.

PHONE NO: 615-483-8611, ext. 3-6760

**Presented at the American Society of Agronomy Annual Meeting, Held at Knoxville, TN, August 24-31, 1975**

**LEAD; CADMIUM; SHELTERS; SHELTER-CONTAMINATED FOREST SOIL; SOILS; FOREST**

**Behavior of Pb and Cd in a Shelter-Contaminated Forest**

Bondietti, E.A.; Jackson, D.R.; Sweeton, F.H.

PHONE NO: 615-483-8611 ext. 3-6760

**Presented at the International Conference on Heavy Metals in the Environment, Toronto, Ontario, Canada, October 27-31, 1975**

**LEAD; CADMIUM; SHELTERS; SHELTER-CONTAMINATED FOREST; FOREST**

**Spark-Source Mass Spectrometric Techniques for the Analysis of Lanthanide and Actinide Elements in Microgram and Sub-Microgram Transuranium Samples**

Carter, J.A.; Cameron, A.E.; Dean, J.A.

PHONE NO: 615-483-8611, ext. 3-5463

**Analytical Letters, 8(6), 337-350**

**MASS SPECTROMETRY; ANALYSIS; LANTHANIDE; ACTINIDE; TRANSURANIUM SAMPLES**

**Environmental and Fuel Materials Analyses by Multi-Element Isotope Dilution Spark-Source Mass Spectrometry**

Carter, J.A.; Donohue, D.L.; Franklin, J.C.; Stelzner, R.W.

PHONE NO: 615-483-8611, ext. 3-5463

**Presented at the 9th Annual Conference on Trace Substances in Environmental Health, Held at University of Missouri, Columbia, Missouri, June 10-12, 1975**

**FUEL; ANALYSIS; ISOTOPE DILUTION; MASS SPECTROMETRY**

**Trace Impurities in Fuels by Isotope Dilution Mass Spectrometry**

Carter, J.A.; Walker, R.L.; Sites, J.R.

PHONE NO: 615-483-8611, ext. 3-5463

**Advances in Chemistry Series, No. 141, Trace Elements in Fuel, pp. 74-83.**

**IMPURITIES; FUEL; ISOTOPE DILUTION; MASS SPECTROMETRY**

**An Ion Microprobe Investigation of the Tensile Failure of a Pt-Rh-W Alloy Caused by Segregation of Silicon to Grain Boundaries**

Christie, W.H.; Smith, D.H.; Inouye, H.

PHONE NO: 615-483-8611, ext. 3-7168

**Presented at Seminar on Quantitative Techniques in Secondary Ion Mass Spectrometry, Held at Honolulu, Hawaii, October 13-17, 1975**

**ION MICROPROBE; SEGREGATION; SILICON; GRAIN BOUNDARIES; ALLOYS**

**NSF-BANN Trace Contaminants Abstracts**

Copenhaver, E.D. (ed.)

PHONE NO: 615-483-8611, ext. 3-0284

**ORNL-EIA-75-60, Vol. 2, Nos. 1-3, Vol. 3, No. 1, Oak Ridge National Laboratory, Oak Ridge, TN 37830**

**TRACE ELEMENTS; METALS; BIBLIOGRAPHY**

**Standard Deviation as a Function of Time; Three Hours to Five Hundred Seventy-Six Hours**

Culkowski, W.H.

PHONE NO: 615-483-8611, ext. 3-4301

**U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, ATDL Contribution File No. 75/11, 8 p.**

**STANDARD DEVIATION; WIND; HORIZONTAL WIND; MODELING; POINT SOURCE EMISSIONS; PLUMES; DISPERSION; POWER LAW**

**Validation of a Multi-Source Dispersion Model for Atmospheric Sulfur Concentrations**

Culkowski, W.M.; Patterson, M.R.

PHONE NO: 615-483-8611, ext. 3-4301

Presented at the AGU Conference, Held at San Francisco, CA, Dec. 10-12, 1974

ATMOSPHERIC TRANSPORT; SULFUR; VALIDITY; STABILITY; POINT SOURCES; MULTI-SOURCE DISPERSION MODEL; ATMOSPHERE; MODELS; MODELING; PLUMES; STEAM PLANT; CCAL; WETFALL; DRYFALL; HYDROLOGIC TRANSPORT MODEL

**A Comprehensive Atmospheric Transport and Diffusion Model**

Culkowski, W.M.; Patterson, M.R.

PHONE NO: 615-483-8611, ext. 3-4301

ORNL-NSF-EATC 17 (In Press)

ATMOSPHERIC TRANSPORT; DEPOSITION; WASHOUT; POINT SOURCES; AREA SOURCES; LINE SOURCE; STABILITY; MODELS; MODELING; ATMOSPHERIC TRANSPORT MODEL; DIFFUSION MODEL; DIFFUSION

**Environmental Data Extraction: An Experiment in Tabular Data Extraction from Primary Sources**

Dailey, G.A.; Copenhagen, E.D.

PHONE NO: 615-483-8611, ext. 3-0284

In Preparation

DATA EXTRACTION; TABULAR DATA EXTRACTION; BIOLOGICAL UPTAKE; BIOLOGICAL ELIMINATION; TRANSPORT; ABATEMENT; DISPOSAL; PERSISTENCE; ANALYTICAL METHODOLOGY; ENVIRONMENTAL MONITORING; CRITERIA; STANDINGS

**Analysis of Seasonal Leaf Fall in North Temperate Deciduous Forests**

Dixon, K.R.

PHONE NO: 615-483-8611, Ext. 3-6361

Submitted to Cikos

LEAF FALL; LITTERFALL; MODELS; DECIDUOUS FORESTS; TREES; FORESTS

**A Simulation of the Effect of Thermal Plumes on the Mercury Dynamics of Zooplankton**

Dixon, K.R.

PHONE NO: 615-483-8611, ext. 3-6361

Presented at the International Conference on Heavy Metals in the Environment, Held at Toronto, Ontario, Canada, October 27-31, 1975

SIMULATION; MODELS; MODELING; ZOOPLANKTON; THERMAL PLUMES; MERCURY; UPTAKE; ELIMINATION

**CHNSEI: Simulation of Sediment and Trace Contaminant Transport with Sediment/Contaminant Interaction**

Fields, D.E.

PHONE NO: 615-483-8611, 3-1615

ORNL-NSF-EATC 19, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 1975, October

SEDIMENTS; EXCHANGE; SIMULATION; MATHEMATICAL MODELS; MODELING; HYDROLOGY; UNIFIED TRANSPORT MODEL; BED LOAD; SUSPENDED LOAD; TRANSPORT; VALIDATION; MODELS

**A Simulation of Trace Contaminant Transport Through a Channel System with Chemical Exchange Between Sediment and Water**

Fields, D.E.

PHONE NO: 615-483-8611, Ext. 3-1615

Presented at Fall Annual Meeting of American Geophysical Union, San Francisco, California, December 1974

SIMULATION; EXCHANGE; SEDIMENTS; HYDROLOGY; MATHEMATICAL MODELS; BED LOAD; SUSPENDED LOAD; TRANSPORT; UNIFIED TRANSPORT MODEL; TRANSPORT MODELS; MODELS

**Computer Simulation of Mass Transport on Walker Branch Watershed, Oak Ridge, Tennessee. Part I. Water and Sediment Transport**

Fields, D.E.; Haridon, R.J.

PHONE NO: 615-483-8611, Ext. 3-1615

Presented at the Tennessee Academy of Science, Held at Memphis, Tennessee, November 22, 1974

HYDROLOGY; SEDIMENTS; TRANSPORT; MODELING; MATHEMATICAL MODELS; BED LOAD; SUSPENDED LOAD; DYNAMICS; SIMULATION; UNIFIED TRANSPORT MODEL; TRANSPORT MODELS; MODELS

**OPTRM - A Hydrologic Transport Model with Parameter**

Fields, D.E.; Watson, S.B.

PHONE NO: 615-483-8611, Ext. 3-1615

ORNL-NSF-EATC 14, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 130 p.; 1975, September

UNIFIED TRANSPORT MODEL; OPTIMIZATION; HYDROLOGY; TRANSPORT; CONTAMINANTS; WATERSHED; MODELING; SIMULATION; MATHEMATICAL MODELS; TRANSPORT MODELS; MODELS

**Multi-Element Isotope Dilution Spark-Source Mass Spectrometry**

Franklin, J.C.; Carter, J.A.; Donohue, D.L.; Stelzner, R.W.

PHONE NO: 615-483-8611, ext. 3-7168

Presented at the 23rd Annual Conference on Mass Spectrometry and Allied Topics, Held at Houston, Texas, May 11-16, 1975

SPARK-SOURCE MASS SPECTROMETRY; MASS SPECTROMETRY; ISOTOPE DILUTION



**Chlorine-Containing Stable Organics: New Compounds of Environmental Concern**

Gehrs, C.W.; Jolley, R.L.

PHONE NO: 615-483-8611, Ext. 3-6617

Proceedings of the 19th Congress of the International Association of Limnology, Held at Winnipeg, Manitoba, August 22-29, 1974

AQUATIC POLLUTION; CHLORO-ORGANICS; CHLORINATION; NATURAL WATERS; HIGH-RESOLUTION; LIQUID CHROMATOGRAPHY; TOXICITY; CHLORINE

**Chemical Fractionation and Multicomponent Gas Chromatographic Analysis of Coal-Derived Liquids**

Guerin, H.R.

PHONE NO: 615-483-8611, Ext. 3-6901

Presented at "Confab 75", The Fossil Fuel Chemistry and Energy Conference, Held at Laramie, Wyoming, July 22-26, 1975

FRACTIONATION; GAS CHROMATOGRAPHY; COAL-DERIVED LIQUIDS; CHEMISTRY; ANALYSIS

**Chemical Characterization of Coal Conversion Pilot Plant Materials**

Guerin, H.R.; Griest, W.H.; Ho, C.H.; Shultz, W.D.

PHONE NO: 615-483-8611, Ext. 3-6901

To be published in Proceedings of the Third ERDA Environmental Protection Conference, Held at Chicago, Illinois, September 23-26, 1975

COAL DERIVED MATERIALS; GAS CHROMATOGRAPHY; CARCINOGENS; COAL CONVERSION

**Distribution and Bioaccumulation of Mercury in Biotic and Abiotic Compartments of a Contaminated River-Reservoir System**

Hildebrand, S.G.; Andren, A.W.; Huckabee, J.W.

PHONE NO: 615-483-8611, ext. 3-1410

Proceedings of the Workshop, Toxicity to Biota of Metal Forms in Natural Waters, International Joint Commission, Great Lakes Research Advisory Board, Duluth, MN, October 1975 (In Press)

MERCURY; FISH; RIVERS; INVERTEBRATES; WATER; SEDIMENTS; DISTRIBUTION; BIOACCUMULATION; RESERVOIRS

**Studies of the Contributions of Nonpoint Terrestrial Sources to Mineral Water Quality**

Huff, D.D.

PHONE NO: 615-483-8611, Ext. 3-6650

Proceedings of the NRC/TIE Joint Panel on Ecosystem Analysis (Workshop), Held at Austin, Texas, 1975

WATER QUALITY; AQUATIC ECOSYSTEMS; NONPOINT SOURCES; MODELS; TRANSPORT; HYDROLOGY; TRANSPORT MODELS

**Cadmium Activity in Soils: An Evaluation of a Cd Ion Selective Electrode**

Jackson, D.R.; Bondietti, E.A.

PHONE NO: 615-483-8611, Ext. 3-6804

Soil Science Society of America, Proceedings, (In Press)

CADMIUM; SOILS; METALS; ION ELECTRODES; ANALYSIS

**Extraction of Soil Water Using Cellulose Acetate Hollow Fibers**

Jackson, D.R.; Brinkley, F.S.; Bondietti, E.A.

PHONE NO: 615-483-8611, Ext. 3-6804

Soil Science Society of America, Proceedings, (In Press)

SOIL WATER; CADMIUM; SOILS; SOIL WATER EXTRACTION; EXTRACTION; FIBERS; CELLULOSE ACETATE; FIBERS

**Disruption of Macronutrient Pools in Forest-Floor Litter Near a Lead Smelter**

Jackson, D.R.; Watson, A.P.

PHONE NO: 615-483-8611, Ext. 3-6804

In Review

FOREST NUTRIENTS; FORESTS; NUTRIENTS; FOREST LITTER; LITTER; LEAD SHELTERS; LEAD; SHELTERS; LEAF LITTER

**Chlorine-Containing Organic Constituents on Chlorinated Effluents**

Jolley, R.L.

PHONE NO: 615-483-8611, Ext. 3-1940

J. Water Pollution Control Federation, 47, 601-618

HIGH-RESOLUTION LIQUID CHROMATOGRAPHY; RADIOACTIVE TRACERS; CHLORINATION; DISSOLVED ORGANICS; WATER POLLUTION; ANALYSIS; CHLORINATED EFFLUENTS

**Chlorination of Cooling Water: A Source of Chlorine-Containing Organic Compounds with Possible Environmental Significance**

Jolley, R.L.; Gehrs, C.W.; Pitt, W.W., Jr.

PHONE NO: 615-483-8611, Ext. 3-1940

Proceedings of the Fourth National Symposium on Radiocology, Held at Corvallis, Oregon, May 17-18, 1975

CHLORINATION; PROCESS COOLING WATERS; CHLORO-ORGANICS; WATER POLLUTION; CHLORINE 36; AQUATIC ECOSYSTEMS; ANALYSIS; HIGH-RESOLUTION LIQUID CHROMATOGRAPHY

Determination of Chlorination Effects on Organic Constituents in Natural and Process Waters Using High-Pressure Liquid Chromatography

Jolley, R.L.; Jones, G., Jr.; Thompson, J.E.

PHONE NO: 615-483-8611, Ext. 3-1940

Presented at the First Chemical Congress of the North American Continent, Held at Mexico City, Mexico, Nov. 30-Dec. 5, 1975

CHLORINATION; NATURAL WATERS; PROCESS COOLING WATERS; SEWAGE EFFLUENTS; CHLORO-ORGANICS; HIGH-RESOLUTION LIQUID CHROMATOGRAPHY; CHLORINE 36; ANALYSIS; WATER; LIQUID CHROMATOGRAPHY; PROCESS WATER

Soluble Organic Constituents in Sewage Treatment Plant Effluents as Determined by a Multicomponent Analytical Technique

Jolley, R.L.; Pitt, W.W., Jr.; Rainey, W.T., Jr.

PHONE NO: 615-483-8611, Ext. 3-1940

Presented at the 169th National Meeting of the American Chemical Society, Division of Environmental Chemistry, Held at Philadelphia, PA, 75(1), 221-224, 1975

SEWAGE PLANT EFFLUENTS; WATER POLLUTION; ANALYSIS; HIGH-RESOLUTION LIQUID CHROMATOGRAPHY; POLLUTANT IDENTIFICATION; ORGANIC POLLUTANTS; SOLUBLE ORGANIC CONSTITUENTS; SEWAGE TREATMENT PLANT; SEWAGE TREATMENT

Analysis of Soluble Organic Constituents in Natural and Process Waters by High-Pressure Liquid Chromatography

Jolley, R.L.; Pitt, W.W., Jr.; Scott, C.P.; Jones, G., Jr.; Thompson, J.E.

PHONE NO: 615-483-8611, Ext. 3-1940

Presented at the 9th Annual Conference on Trace Substances in Environmental Health, Held at Columbia, Missouri, June 10-12, 1975

ANALYSIS; SOLUBLE ORGANIC CONSTITUENTS; NATURAL WATERS; PROCESS WATER; WATER; HIGH-PRESSURE LIQUID CHROMATOGRAPHY; LIQUID CHROMATOGRAPHY

Pathways of Thirty-Seven Trace Elements Through Coal-Fired Power Plant

Klein, D.E.; Andren, A.W.; Carter, J.A.; Emery, J.F.; Feldman, C.; Fulkerson, W.; Lyon, W.S.; Ogle, J.C.; Talmi, Y.; Van Hook, R.I.; Bolton, R.E.

PHONE NO: 615-483-8611, Ext. 3-6977 (R.I. Van Hook)

Environmental Science and Technology, 9(10), 973-979

TRACE ELEMENTS; COAL-FIRED POWER PLANTS; POWER PLANTS; COAL; FLY ASH; SLAG; COMBUSTION GASES; GASES; SAMPLING; ANALYSIS; CADMIUM; ARSENIC; COPPER; LEAD; SELENIUM; ZINC; MOLYBDENUM; TIN

Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples

Kubota, H.; Griest, W.H.; Guerin, M.R.

PHONE NO: 615-483-8611, Ext. 3-6901

To be published in Proceedings of the 9th Annual Conference on Trace Substances in Environmental Health, Held at Columbia, Missouri, June 9-12, 1975

CARCINOGENS; TOBACCO SMOKE; COAL-DERIVED LIQUIDS; GAS CHROMATOGRAPHY; ANALYSIS; TOBACCO; SMOKE; COAL

Analytical Analysis of Soil-Moisture and Trace-Contaminant Transport

Larsen, M.E.; Reeves, M.

PHONE NO: 615-483-8611, Ext. 3-1724

ORNL-NSF-EATC-12, Oak Ridge National Laboratory, Oak Ridge, Tennessee, (In Preparation)

SOIL MOISTURE; TRANSPORT; MODELS; HYDROLOGY; ANALYSIS; MOISTURE; SOILS; TRANSPORT MODELS

Heavy Metals and Other Trace Elements

Leland, H.V.; Copenhagen, E.D.; Wilkes, D.J.

PHONE NO: 615-483-8611, ext. 3-0284

J. of Water Pollution Control Federation, 47(6), 1635-1656

TRACE ELEMENTS; AQUATIC ECOSYSTEMS; REVIEW; METALS; TRANSPORT; CONCENTRATION; WATER POLLUTION CONTROL; NATURAL WATERS; HUMAN HEALTH; SEDIMENTS; BIOCHEMICAL TRANSFORMATIONS; ACCUMULATION; TOXICITY; FLORA; FAUNA; POLLUTION SOURCES; FISH; WATER

Mass Balance of Trace Elements in Walker Branch Watershed - The Relation to Coal Fired Steam Plants

Lindberg, S.E.; Andren, A.W.; Baridon, R.J.; Fulkerson, W.

PHONE NO: 615-483-8611, Ext. 3-1283

Presented at the Third Annual Research Triangle Conference on Heavy Metals in the Environment, Chapel Hill, North Carolina, May 15-16, 1975. To be published in Environmental Health Perspectives.

TRACE ELEMENTS; WATERSHED; COAL FIRED POWER PLANTS; POWER PLANTS; MASS BALANCE

Soil-Plant-Water Effects on Uptake and Movement of Contaminants

Luxmoore, R.J.; Huff, D.D.; Dixon, K.R.

PHONE NO: 615-483-8611, Ext. 3-6432

Proceedings of the Second Annual Trace Contaminants Conference, Held at Asilomar, CA, June 2-6, 1975

SOIL-PLANT-ATMOSPHERE SYSTEM; SIMULATION MODELS; UPTAKE; MOVEMENT; SOILS; PLANTS; WATER; MODELS; SOLUTE UPTAKE; SOLUTE TRANSPORT

**Soil-Plant-Water Relations of Tulip Poplar Forest on Podsolized Soil**

Luxmoore, R.J.; Buff, D.D.; McConathy, R.K.; Dinger, B.E.

PHONE NO: 615-483-8611, Ext. 3-6432

Presented at the 1974 Annual American Society of Agronomy, Held at Chicago, Illinois, November 10-15, 1974

WATER FLUX; EVAPOTRANSPIRATION; STOMATA; WATER POTENTIAL; SIMULATION MODELS; TULIP POPLAR; FOREST; PODSOLIZED SOIL; SOILS; PLANTS; WATER; TRANSPORT MODELS

**The Hydrolysis of Cations, A Critical Review of Hydrolytic Species and Their Stability Constants in Aqueous Solution**

Mesner, R.E.; Baes, C.F., Jr.

PHONE NO: 615-483-8611, ext. 3-1447 or 3-6262

ORNL-NSF-EATC-3, Part I-IV, (Part IV still in press), Oak Ridge National Laboratory, Oak Ridge, TN 37830

HYDROLYSIS; SPECIES; METAL IONS; REVIEW; AQUEOUS SOLUTIONS

**Solvent Extraction of Organomercury Compounds**

Moore, F.L.

PHONE NO: 615-483-8611, Ext. 3-6420

Environmental Letters, 10(2), 1975

SOLVENT EXTRACTION; ORGANOMERCURY COMPOUNDS

**Solvent Extraction of Cadmium from Alkaline Cyanide Solutions with Quaternary Amines**

Moore, F.L.

PHONE NO: 615-483-8611, Ext. 3-6420

Environmental Letters, 10(1), 1975

SOLVENT EXTRACTION; CADMIUM; CYANIDE SOLUTIONS; QUATERNARY AMINES

**Liquid-Liquid Extraction of Zinc with High-Molecular-Weight Amines from Alkaline Cyanide Solutions**

Moore, F.L.

PHONE NO: 615-483-8611, Ext. 3-6420

Separation Science, 10(4), 489

LIQUID-LIQUID EXTRACTION; SOLVENT EXTRACTION; ZINC; CYANIDE SOLUTIONS

**Modeling the Transport of Lead in the Vicinity of a Lead Mine-Smelter Complex in Missouri**

Munro, J.K.

PHONE NO: 615-483-8611, Ext. 3-6264

Presented as Part of ORAU Summer Course for College teachers on Applied Ecology, 30 July 1975. Same lecture also presented on 27 February 1975 at Tougaloo College, Jackson, Mississippi as

**part of ORAU Traveling Lecture Program**

ATMOSPHERIC TRANSPORT; HYDROLOGIC TRANSPORT; DEPOSITION RATES; DIGITAL SIMULATION; SOILS; LITTER; LEAD; CHEMICAL EXCHANGE; PLANT UPTAKE; SULFUR DIOXIDE; CADMIUM; COPPER; ZINC; WATERSHED; LEAD MINES; SHELTERS; EMISSION RATES; STACKS; POINT SOURCES; AREA SOURCES; SURFACE RUNOFF; TRANSPORT MODELS; MODELS; UNIFIED TRANSPORT MODEL

**The Use of Simulation Models as a Tool for Ecological Research**

Munro, J.K.

PHONE NO: 615-483-8611, Ext. 3-6264

Presented as part of ORAU Summer Course for college teachers on Applied Ecology, July 1975. Same lecture also presented on 17 January 1975 at Wheaton College, Wheaton, Illinois and on 27 February 1975 at Tougaloo College, Jackson, Mississippi as part of ORAU Travelling Lecture Program

DIGITAL SIMULATION; COMPUTER MODELING; ECOSYSTEM MODELS; TRANSPORT; RESIDENCE TIMES; ACCUMULATION; FEEDBACK; INPUT; OUTPUT; PARAMETERS; DECISION MAKING; FOOD CHAINS; TRANSPORT MODELS; MODELS

**Simulation of Lead Transport on the Crooked Creek Watershed**

Patterson, H.R.; Munro, J.K.; Luxmoore, R.J.

PHONE NO: 615-483-8611, Ext. 3-6502

Presented at Trace Substances Conference Held in Columbia, Missouri, June 9-12, 1975

TRANSPORT MODELS; METALS; ATMOSPHERIC TRANSPORT; LEAD; WETFALL DEPOSITION; DRYFALL DEPOSITION; SURFACE EMISSION; PARTICULATES; ORE; SLAG; LITTER; SOILS; STACKS; PARTICLE SIZE; WINDROSE; SHELTERS; EMISSIONS; POINT SOURCES; AREA SOURCES; MODELS

**Separation and Analysis of Refractory Pollutants in Water by High-Resolution Liquid Chromatography**

Pitt, W.W., Jr.; Jolley, R.L.; Katz, S.

PHONE NO: 615-483-8611, Ext. 3-6676

Presented at the First Chemical Congress of the North American Continent, Held at Mexico City, Mexico, Nov. 30-Dec. 5, 1975

WATER; REFRACTORY ORGANIC POLLUTANTS; ANALYSIS; HIGH-RESOLUTION LIQUID CHROMATOGRAPHY; LIQUID CHROMATOGRAPHY; SEWAGE EFFLUENTS; NATURAL WATERS; COAL LIQUEFACTION; AQUEOUS WASTES; SEPARATION; WATER

**Computer Simulation of Trace Metal Transport**

Ravitsky, R.J.; Andren, A.W.

PHONE NO: 615-483-8611, Ext. 3-1213

Presented at the International Conference on Heavy Metals in the Environment, Toronto, Canada, October 27-31, 1975

MODELING; WATER BUDGET; POTASSIUM; SIMULATION; TRANSPORT; CADMIUM; METALS; TRANSPORT MODELS; MODELS

Computer Simulation of Mass Transport on Walker Branch Watershed, Oak Ridge, Tennessee. Part II. Trace Element Transport

Raridon, R.J.; Fields, D.E.

PHONE NO: 615-483-8611, Ext. 3-1213

Presented at the Tennessee Academy of Science, Memphis, Tennessee, November 22, 1974

MODELING; WATER BUDGET; POTASSIUM; SIMULATION; TRANSPORT; TRANSPORT MODELS; TRACE ELEMENTS; MODELS

Computer Simulation of Potassium Transport on Walker Branch Watershed

Raridon, R.J.; Henderson, G.S.

PHONE NO: 615-483-8611, Ext. 3-1213

Presented at the 1974 Annual Meeting American Society of Agronomy, Chicago, Illinois, November 10-15, 1974

MODELING; ENVIRONMENTAL MONITORING; WATER BUDGET; POTASSIUM; SIMULATION; WATERSHEDS; TRANSPORT MODELS; TRANSPORT; MODELS

Quantitative X-Ray Fluorescent Analysis Using Fundamental Parameters

Sparks, C.J.

PHONE NO: 615-483-8611, ext. 3-1941

Part of Gould, R.W.; Barrett, C.S.; Newkirk, J.B.; Ruud, C.O. (eds.), X-Ray Analysis, Plenum Press, NY, Vol. 19; Presented at the 24th Annual Conference on Applications of X-Ray Analysis, Held at Denver, CO, August 6-8, 1975

ANALYSIS; X-RAY FLUORESCENT ANALYSIS; X-RAY FLUORESCENCE; FUNDAMENTAL PARAMETERS

The Determination of Arsenic and Arsenicals

Talmi, Y.; Bostick, D.T.

PHONE NO: 615-483-8611, Ext. 3-1506 (W.D. Shultz)

J. Chrom. Sci., 13, 231

ARSENIC; ARSENICALS; GC/HES; GAS CHROMATOGRAPHY; MICROWAVE EMISSION; ANALYSIS

Determination of Alkylarsenic Acids in Pesticide and Environmental Samples by Gas Chromatography with a Microwave Emission Detector System

Talmi, Y.; Bostick, D.T.

PHONE NO: 615-483-8611, Ext. 3-1506 (W.D. Shultz)

Anal. Chem., 1975, (In Press)

ALKYLARSENIC ACIDS; PESTICIDES; ENVIRONMENTAL SAMPLES; GC/HES; GAS CHROMATOGRAPHY; MICROWAVE EMISSION; ANALYSIS

The Determination of Traces of Arsenic: A Review

Talmi, Y.; Feldman, C.

PHONE NO: 615-483-8611, ext. 3-1233

Part of Woolson, E.A. (ed.), Arsenical Pesticides, ACS Symposium Series, No. 7, 1975

ARSENIC; PESTICIDES; ANALYSIS; DETERMINATION; ARSINE; GAS CHROMATOGRAPHY; ATOMIC ABSORPTION; WET-ASHING; REVIEW

A Rapid Method for the Determination of  $\text{CH}_3\text{HgCl}$  at the Part Per Trillion Level in Water Samples Using the Gas Chromatograph-Microwave Emission Spectrometric Detector System

Talmi, Y.; Norwell, V.E.

PHONE NO: 615-483-8611, Ext. 3-1506 (W.D. Shultz)

Submitted to Anal. Chem., Sept. 1975

WATER; GC/HES; METHYLMERCURIC CHLORIDE; GAS CHROMATOGRAPHY; MICROWAVE EMISSION; SPECTROMETRY; ANALYSIS

Digital Topography; Calculation of Watershed Area and Slope

Tucker, T.C.; Fields, D.E.

PHONE NO: 615-483-8611, Ext. 3-1211

ORNL-NSF-EATC-20, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 1975, October

TOPOGRAPHY; WATERSHED; SLOPES; MODELING; MODEL INTERPOLATION; STREAMS; UNIFIED TRANSPORT MODEL; HYDROLOGY; SIMULATION; WATERSHED; MODELS

Trace Element Impact on Forest Floor Litter in the New Lead Belt Region of Southeast Missouri

Watson, A.F.

PHONE NO: 615-483-8611, Ext. 3-0298

Presented at the Ninth Annual Conference on Trace Substances in Environmental Health, Held at Columbia, Missouri, June 9-12, 1975

LITTER; DECIDUOUS FORESTS; TRACE ELEMENTS; METALS; CADMIUM; LEAD; ZINC; COPPER; DECOMPOSITION; LITTER MASS; WATERSHEDS; LEAF LITTER

Toxicity of Organic and Inorganic Arsenicals to an Insect Herbivore

Watson, A.F.; Van Hook, R.I.; Reichle, D.E.

PHONE NO: 615-483-8611, Ext. 3-0298

Accepted for Publication in Environmental Science and Technology

ARSENICALS; ORGANIC ARSENICALS; INORGANIC ARSENICALS; CACODYLIC ACID; SODIUM CACODYLATE; ARSENIC TRIOXIDE; ARSENIC PENTOXIDE; MEADOW RATYDIDS; NON-TARGET SPECIES; TOXICITY; LD50; LETHAL DOSE; INSECTS

**NST-RANN Trace Contaminants Directory**

Wilkinson, B.R.; Smith, S.K.

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ORNL-RIS-75-62, Oak Ridge National Laboratory,  
Oak Ridge, TN 37830, 1975, November

A directory listing the participants in the  
National Science Foundation, Research Applied to  
National Needs Trace Contaminants Program, by  
name, address, telephone number and a brief  
description of research interests.



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